CANADIAN
JOURNAL OF RESEARCH

CONTENTS

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

THERMAL STRESS IN LONG CYLINDRICAL SHELLS DUE TO TEMPERATURE VARIATION ROUND THE CIRCUMFERENCE, AND THROUGH THE WALL[1]

BY J. N. GOODIER[2]

Abstract

The thermal stress in thin-walled cylinders of any cross section has been investigated for internal and external temperatures each varying in any manner round the circumference but not in the axial direction. The thickness also may vary round the circumference.

A method is given for calculating the stress from given temperature distributions, whatever the shape of the cross section. The stress is evaluated for uniform, but different, inside and outside temperatures.

The circular cylinder is treated in detail and the stress found for the general case of circumferential variation. It is shown that the maximum stress will depend only on the temperature distributions and the material, and not on the thickness or diameter of the cylinder.

1. The problems of thermal stress, that is, stress due to non-uniform heating, like the ordinary problems of stress and strain in elastic bodies, fall into two groups. The first group can be satisfactorily treated only by solution of the fundamental differential equations of elasticity for appropriate boundary conditions.* The second group consists of those problems which can, for practical purposes, be adequately treated by the approximate but simple and convenient formulas of the subject usually described as the strength of materials. The well-known Bernoulli-Euler formula for the bending of beams is typical of these. The simplification arises from the circumstance of one or two dimensions of the shapes considered—beams, thin plates, and thin shells—being small.

Some of these simple formulas will be employed to solve the problem described by the title of this paper. Temperatures varying along the axis, but not round the circumference, and temperatures uniform, but different, inside and outside a cylinder, have been dealt with by previous writers (4, 6), but only for the particular case of the circular tube. The thin tube of any shape, with completely general variation of temperature over the surfaces, presents a problem of great analytical difficulty. The differential equations involved are not linear. The same is true of the flat plate with general

---

surface temperatures. The restricted problem we are concerned with, however, is not only important in engineering, notably in its application to boiler tubes, but also tractable mathematically.

We begin with the incomplete cylinder, *i.e.*, the section $AQPFC$, Fig. 1, is not a closed curve. The results obtained are necessary for the complete cylinder, which, for the present, is supposed converted into an incomplete one by a cut along a generator, equivalent to a gap of zero width. The
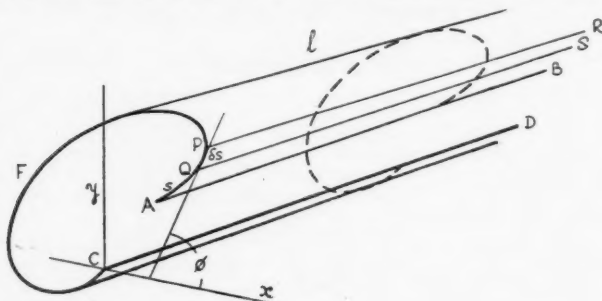
FIG. 1.

problem is reduced, by a physical argument, to the solution of a set of equations. A narrow strip $PQSR$ is considered in isolation. It is given arbitrary inside and outside temperatures, T_i and T_e respectively (the transition through the thickness being linear), while the remainder of the tube is kept unheated. The strip expands, bends and curls, and no longer fits the place from which it was taken. But by the imposition of suitable terminal forces and couples it is so far restored to its original state that it can be supposed reattached to the rest of the tube, so that points originally contiguous are so again without any necessity for straining the rest of the tube. The reassembly, however, involves relative rigid body displacements of the two cold parts PFC and QA, and hence an alteration of the gap AC. This alteration is calculated. Then the stress system required to re-close the gap AC, if the tube be a closed one, is found, and the effects of removing the imposed terminal forces and couples of the strip are considered. The effects of heating over more than an elementary strip follow by integration.

The Incomplete Cylinder

2. For the moment, let the strip $PQSR$ (Figs. 1 and 2) of (the complete) axial length l and infinitesimal arc length δs, have the inside temperature T_i, and outside temperature T_e, the rest of the cylinder being kept at temperature zero.

Let this strip be freed from the rest of the cylinder by cuts along PR and QS. Then it is free to expand, without thermal stress.* It increases its linear dimensions, and also changes its curvature on account of the tem-

---

* *There is a general theorem that temperature distributions linear in cartesian co-ordinates give rise to no stress (8, p. 204).*

perature gradient through the thickness. If the mean temperature $T_m = \frac{1}{2}(T_i + T_e)$, then the length increases by a uniform linear strain αT_m, i.e., by $l\alpha T_m$, α being the coefficient of linear expansion. The arc length δs increases by $\delta s \cdot \alpha T_m$. The thickness h increases by $h\alpha T_m$. The length l, which originally had no curvature, becomes curved, as sketched in Fig. 2 (with $T_e > T_i$), to a radius r, where $1/r = (T_e - T_i)\alpha/h$.
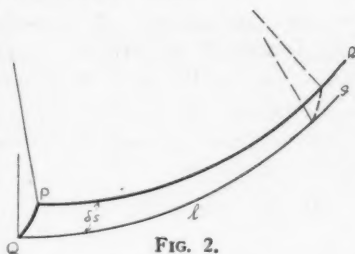
FIG. 2.

The arc δs changes its curvature by the same amount.

3. A compressive stress $E\alpha T_m$, applied to the ends of the strip will exactly cancel the thermal strain αT_m in the direction l (where E is Young's modulus). It will increase δs by a strain $\sigma \alpha T_m$ (where σ is Poisson's ratio) so that the total increase of δs becomes $\delta s(1 + \sigma)\alpha T_m$. It will also increase the thickness h by $h\sigma\alpha T_m$.

A bending moment of suitable magnitude, applied to the ends, will exactly cancel the thermal curvature of l, $(T_e - T_i)\alpha/h$. It is easily found from simple beam formulas that the necessary bending moment is $\frac{1}{12}E\alpha h^2(T_e - T_i)\delta s$. The vector representing this moment is in the direction of δs.

This moment will produce an *anticlastic* curvature of δs, of amount $\sigma(T_e - T_i)\alpha/h$, and the total change of curvature of δs is therefore now $(1 + \sigma)(T_e - T_i)\alpha/h$.

The edges PR and QS of the strip are at present thicker than the thickness h of the cold tube by $h(1 + \sigma)\alpha T_m$. In order to bring the faces of the cuts of the strip and of the rest of the tube to the same configuration, it must be supposed that shearing and normal tractions as indicated in Fig. 3, and perhaps others, act on the strip, and equal and opposite tractions on the rest of the tube.
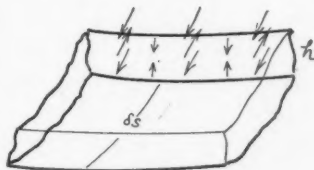
FIG. 3.

It is however neither practicable nor necessary to compute these tractions and their effects. The strip, at present, is regarded as hot, and the rest of the tube as cold. But later the effects of heating all such strips will be added so as to arrive at a tube heated all round, the temperature varying smoothly. Evidently the adjustment of the thickness of one strip to that of its neighbors involves only the temperature differentials. In the limit, therefore, the required tractions on the cuts such as PR and QS will vanish. We may say that they disappear in the process of integration.*

* The validity of this argument may be better seen by considering a problem of plane stress. Let a long strip be compressed on finite opposite segments on the two edges. The part between these segments may be considered in isolation, and we may inquire what tractions are necessary to fit it back into the strip. We should find that an adjustment of thickness is required, just as in the present problem. But if the compressive forces have a smooth distribution over a succession of infinitesimal segments, the process of integration involved eliminates the tractions that have to be introduced to adjust the thickness, and the stress is plane. This is confirmed by the exact analytical solution of the plane stress problem.

4. For the present, suppose that the tractions act, so that the thicknesses become equal. Any other possible effects due to the tractions on the strip need not be considered. Then we may suppose that the strip is rejoined to the other two parts of the cylinder. But on account of the alterations in the length and curvature of δs, these parts will no longer have their former relative positions.

Consider any cross section of the cylinder and draw rectangular axes Cx, Cy with origin on CD. In Fig. 1 these are drawn on the end $AQPFC$, for convenience.

Then the displacement of AQ relative to CFP has x and y components given by,

$$-(1 + \sigma)\alpha T_m \cos \phi \, . \, \delta s - (1 + \sigma)\alpha(T_e - T_i)\frac{y}{h} \delta s$$

and

$$-(1 + \sigma)\alpha T_m \sin \phi \, . \, \delta s + (1 + \sigma)\alpha(T_e - T_i)\frac{x}{h} \delta s \, .$$

The first terms arise from the extension of δs, the second terms from the change in its curvature; the rotation (anticlockwise) of AQ relative to CFP is $-(1 + \sigma)\alpha(T_e - T_i)h^{-1}\delta s$; x and y are the co-ordinates of δs, and ϕ is the angle δs makes with the x-axis.

5. If now all the other strips into which the cylinder may be divided are treated in the same way, each being given its proper temperatures, the displacements δ_x and δ_y and rotation ω of the edge AB relative to the edge CD may be obtained by superposition. Then

$$\left.\begin{aligned}
\delta_x &= -(1 + \sigma)\alpha\int T_m \cos \phi \, . \, ds - (1 + \sigma)\alpha\int (T_e - T_i)\frac{y}{h}ds \, , \\[4pt]
\delta_y &= -(1 + \sigma)\alpha\int T_m \sin \phi \, . \, ds + (1 + \sigma)\alpha\int (T_e - T_i)\frac{x}{h}ds \, , \\[4pt]
\omega &= -(1 + \sigma)\alpha\int (T_e - T_i)\frac{ds}{h} \, ,
\end{aligned}\right\} \quad (1)$$

T_m, T_e and T_i being now given functions of s, the arc length. The integrals are taken all round the section.

These displacements and rotation are maintained by the temperature distribution together with:

(i) Stress $-E\alpha T_m$ on the ends of the cylinder;

(ii) A distribution of moment on the ends,

$$m = \tfrac{1}{12}E\alpha h^2(T_e - T_i),$$

per unit length of arc, the vector of m being directed along δs or along the tangent at any point of the end section.

The state of stress anywhere in the wall of the cylinder is given by the same stress and moment. There is no stress other than the axial component.

6. The end stresses (i) and (ii) of Art. 5 may be eliminated by superposing the ordinary isothermal stress distribution having equal and opposite end stress and moment. The complete determination of this distribution is a problem in the theory of thin shells. However, if the cylinder is long, the distribution in the middle part will depend, according to the Principle of Saint-Venant, only on the *resultant* force and couple on the ends. The resultant force is $E\alpha\int hT_m ds$ and the resultant couple has components

$$
\left.
\begin{aligned}
M_x &= -\tfrac{1}{12}E\alpha\int h^2(T_e - T_i)\cos\phi \cdot ds, \\
M_y &= -\tfrac{1}{12}E\alpha\int h^2(T_e - T_i)\sin\phi \cdot ds,
\end{aligned}
\right\} \tag{2}
$$

and from these the corresponding stress in the middle part can be found from the simple beam theory.

The Complete Cylinder

7. If a cut is made along a generator, the formulas (1) give the displacement and rotation of one face of the cut relative to the other, when the end actions (i) and (ii) of Art. 5 are applied, and the cylinder is heated. The integrals are now taken around the circumference.

The faces of the cut may be brought together by a suitable force and couple on one face, an equal and opposite force and couple on the other face, and rejoined. This introduces an additional stress distribution to be superposed on that of Art. 5.

To evaluate it, consider the forces X_o and Y_o and moment M_o, per unit axial length, distributed uniformly along the faces of the cut, acting on the cut tube (Fig. 4). The displacements and rotation of the face A relative to the face C are conveniently found by Castigliano's theorem (7, p. 434). Since we are dealing with a cylinder and not a ring, we use the plate modulus* $E/(1 - \sigma^2)$ instead of Young's modulus, E, and write D for $Eh^3/12(1 - \sigma^2)$. The thickness h will now be taken as constant, although there would be no difficulty in retaining it as a variable. Then,

FIG. 4.

$$
\left.
\begin{aligned}
D\delta_x &= M_o\int yds + X_o\int y^2ds - Y_o\int xyds \\
D\delta_y &= -M_o\int xds - X_o\int xyds + Y_o\int x^2ds \\
D\omega &= M_o\int ds + X_o\int yds - Y_o\int xds
\end{aligned}
\right\} \tag{3}
$$

The integrals can be expressed in terms of the mean circumference of the section, L, the co-ordinates of the centroid $\bar{x}$, $\bar{y}$, the moments of inertia I_{xx}, I_{yy}, and the product of inertia I_{xy}, of the area of the section, since $L = \int ds$, $L\bar{x} = \int xds$, $L\bar{y} = \int yds$, and $I_{xx} = h\int y^2ds$, $I_{yy} = h\int x^2ds$, $I_{xy} = h\int xyds$. The displacements and rotation given by Equations (3) must be equal and opposite
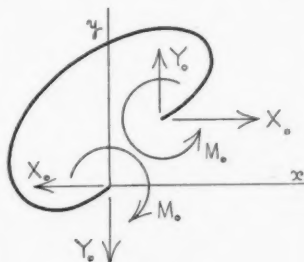
* *Expressing the effect of preventing anticlastic curvature.*

to the displacements and rotation given by Equations (1). The forces X_o and Y_o and the couple M_o can be found by solving the equations,

$$\left. \begin{aligned} M_oLh\bar{y}+X_oI_{zz}-Y_oI_{zy} &= D(1+\sigma)\alpha[h\!\int T_m\cos\phi\,.\,ds+\int(T_e-T_i)yds]\,, \\ -M_oLh\bar{x}-X_oI_{zy}+Y_oI_{yy} &= D(1+\sigma)\alpha[h\!\int T_m\sin\phi\,.\,ds-\int(T_e-T_i)xds]\,, \\ (M_o+X_o\bar{y}-Y_o\bar{x})Lh &= D(1+\sigma)\alpha\!\int(T_e-T_i)ds\,. \end{aligned} \right\}(4)$$

8. The axial stress is made up of four contributions:

(i) A stress $-E\alpha T_m$ (Art. 3);

(ii) A stress corresponding to the distribution of an axial bending moment $\frac{1}{12}E\alpha h^2(T_e-T_i)$ per unit arc length on the mean circumference (Art. 3);

(iii) The axial stress due to the distribution of traction $E\alpha T_m$ on the *ends*. This cancels, on the ends only, the stress (i);

(iv) The axial stress due to the distribution of the couple on the *ends* $-\frac{1}{12}E\alpha h^2(T_e-T_i)$ per unit arc length on the mean circumference. This cancels, on the ends only, the stress (iii).

The ends are then completely free.

The resultant moments of (iv) are given by Equations (2), and the stress due to them, in the middle part, *i.e.*, away from the ends, can be calculated by the simple beam formulas. The appropriate moments of inertia are not I_{zz} and I_{yy} as defined previously, since the latter are referred to axes not through the centroid of the section. Writing I'_{zz}, I'_{yy} for the centroidal moments of inertia, and ζ for the distance normal to the middle surface measured inwards, the stresses (i) to (iv) may be combined into the complete expression for the axial stress

$$E\alpha\left[-T_m+\frac{\zeta}{h}(T_e-T_i)+\frac{1}{L}\!\int T_m ds\right.$$
$$\left.+\frac{h^2(x-\bar{x})}{12I'_{zz}}\!\int(T_e-T_i)\sin\phi\,.\,ds-\frac{h^2(y-\bar{y})}{12I'_{yy}}\!\int(T_e-T_i)\cos\phi\,.\,ds\right]\,(5)$$

When the shape of the cylinder, and the temperature distributions, are given, it is a straightforward process to evaluate the coefficients in Equations (4), analytically or graphically, and to solve for X_o, Y_o and M_o, and from these compute the corresponding stress. The axial stress can be found directly from Expression (5).

Simple formulas can be derived for circular, elliptical, rectangular or other regular sections. The further development, with the exception of the next paragraph, will be confined to the circular case.

Cylinder of Any Shape, but of Uniform Thickness, with Uniform but Unequal Inside and Outside Temperatures

9. It is evident that since the temperature difference is constant around the cylinder, the curvature changes due to it in conjunction with the auxiliary end forces and couples will also be constant around the cylinder. Such a

curvature change can be annulled by a moment distribution M_o. Clearly this is what is required to close the gap. It is easily found that

$$M_o = \frac{\alpha}{h} D(1 + \sigma)(T_e - T_i) .$$

The extreme circumferential stress $(6M_o/h^2)$, then, has the values*

$$\pm \frac{E\alpha(T_e - T_i)}{2(1 - \sigma)} .$$

The complete axial stress is given by (ii) of Art 8, and has the extreme values

$$\pm \tfrac{1}{2} E\alpha(T_e - T_i)$$

except near the ends, which, of course, are free of traction. It is noteworthy that these values are independent of the size, shape and thickness of the cylinder, depending only on the material and the temperatures occurring within it.

It is known that these formulas hold for the special case of the circular tube (8, p. 373).

The Circular Cylinder

10. When the cylinder has a mean radius a, the expressions on the left of the Equations (4) reduce to $\pi a^2 h(2M_o + 3aX_o)$, $\pi a^3 h Y_o$, $2\pi a(M_o + aX_o)$ respectively, with axes as in Fig. 5; in the integrals on the right, ds is replaced by $a\,d\phi$, x by $a \sin \phi$, and y by $a(1 - \cos \phi)$. The solution of the equations is
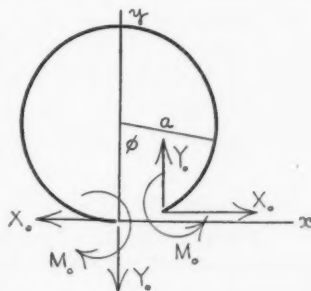
FIG. 5.

$$X_o = \frac{D}{\pi a^2}(1 + \sigma)\alpha \left[\int_0^{2\pi} T_m \cos\phi\,d\phi - \frac{a}{h}\int_0^{2\pi}(T_e - T_i)\cos\phi\,d\phi \right],$$

$$Y_o = \frac{D}{\pi a^2}(1 + \sigma)\alpha \left[\int_0^{2\pi} T_m \sin\phi\,d\phi - \frac{a}{h}\int_0^{2\pi}(T_e - T_i)\sin\phi\,d\phi \right], \qquad (6)$$

$$M_o = \frac{D}{\pi a}(1 + \sigma)\alpha \left[-\int_0^{2\pi} T_m \cos\phi\,d\phi + \frac{a}{2h}\int_0^{2\pi}(T_e - T_i)(1 + 2\cos\phi)d\phi \right].$$

These formulas will give the bending moment, $M_o + X_o y - Y_o x$, per unit axial length, explicitly in terms of the given temperature distributions. The direct stress due to X_o and Y_o will be small, of the order h/a, in comparison with the bending stress.

When the temperature difference $T_e - T_i$ is as great as or greater than the mean temperature $T_m = \tfrac{1}{2}(T_e + T_i)$, the contributions from the latter will be negligible, being of the order h/a, compared with the contributions arising from the temperature difference.

Positive signs pertain to the inside.

11. The integrals occurring in Expression (6) may be replaced by coefficients in the Fourier expansion of T_e and T_i. Let

$$T_e = A_0 + A_1 \cos \phi + A_2 \cos 2\phi + \cdots$$
$$+ B_1 \sin \phi + B_2 \sin 2\phi + \cdots$$
$$T_i = A_0' + A_1' \cos \phi + A_2' \cos 2\phi + \cdots$$
$$+ B_1' \sin \phi + B_2' \sin 2\phi + \cdots$$

Then

$$2\pi A_0 = \int_0^{2\pi} T_e \, d\phi, \quad \pi A_1 = \int_0^{2\pi} T_e \cos \phi \, d\phi, \quad \pi B_1 = \int_0^{2\pi} T_e \sin \phi \, d\phi$$

and A_0', A_1', B_1' are similarly expressed in terms of T_i.

Thus X_o, Y_o and M_o, and the stresses corresponding to them, are independent of the terms in $\cos 2\phi$, $\sin 2\phi$, and all higher harmonics of the temperatures.

Replacing the factors $\frac{a}{h} \pm \frac{1}{2}$ by $\frac{a}{h}$, Equations (6) can be written,

$$\left.\begin{aligned}
X_o &= -\frac{D}{ah}(1 + \sigma)\alpha(A_1 - A_1'), \\
Y_o &= -\frac{D}{ah}(1 + \sigma)\alpha(B_1 - B_1'), \\
M_o &= \frac{D}{h}(1 + \sigma)\alpha[A_1 - A_1' + A_0 - A_0'].
\end{aligned}\right\} \tag{7}$$

To obtain the corresponding extreme fibre stress, neglecting the direct stress due to X_o and Y_o, the moment $M = M_o + X_o y - Y_o x$ is multiplied by $6/h^2$. The result is

$$\pm \frac{E\alpha}{2(1 - \sigma)} \left\{ A_0 - A_0' + (A_1 - A_1') \cos \phi + (B_1 - B_1') \sin \phi \right\} \tag{8}$$

whence the maximum follows easily. This is independent of the radius and thickness of the cylinder.

The complete expression for the axial stress at the middle part of the length is

$$E\alpha \left\{ -T_m + \frac{\zeta}{h}(T_e - T_i) + \frac{1}{2}(A_0 + A_0') \right.$$
$$\left. + (A_1 - A_1') \frac{h}{12a} \cos \phi + (B_1 - B_1') \frac{h}{12a} \sin \phi \right\}. \tag{9}$$

The last two terms will be relatively small. When they are neglected this stress becomes independent of a and h.
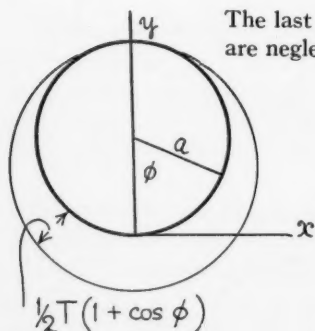
12. As an example of thermal stress in a circular cylinder, let the internal temperature be uniform, and let the external temperature exceed the internal by $\frac{1}{2}T(1 + \cos \phi)$. Then T is the maximum temperature difference, and the distribution of temperature difference round the circumference is as indicated by the polar diagram, Fig. 6. It corresponds roughly to a tube heated from below, and containing a well mixed fluid.

$\frac{1}{2}T(1 + \cos \phi)$

FIG. 6.

A_0 and A_1 are each equal to $\frac{1}{2}T$, and all other Fourier coefficients are zero. Then

$$X_o = -\frac{D}{ah}(1 + \sigma)\alpha\frac{T}{2}, \quad Y_o = 0, \text{ and } M_o = \frac{D}{h}(1 + \sigma)\alpha T.$$

The moment M is given by

$$\frac{D}{h}(1 + \sigma)\alpha T\left(1 - \frac{y}{2a}\right).$$

The maximum is at $y = 0$, and corresponds to an extreme fibre stress

$$\pm E\alpha T/2(1 - \sigma).$$

To obtain a numerical result, take the internal temperature as 100° C., the maximum external temperature as 200° C., E as 3×10^7 lb. per sq. in., α as 11.6×10^{-6} per °C., σ as 0.3 (as for steel). Then $E\alpha T/2(1 - \sigma)$ is nearly equal to 25,000 lb. per sq. in.

The axial stress can be found from Expression (9). With the assumed distribution, there is a compressive stress in the hottest part ($\phi = y = 0$) nearly equal to $\frac{3}{4}E\alpha T$, or 27,000 lb. per sq. in. for the values taken. This is the value for the stress at the inside. At the outside, the axial stress is 9,000 lb. per sq. in. tension.

13. As a final example, let the outside of the cylinder be heated to a temperature T, kept constant over a small arc of circumferential length λ, and let the rest of the outside surface* and the whole inside surface be kept at zero temperature. This is a rough representation of a distribution that might occur in a welding process.

It is easily shown that the maximum circumferential stress is given by

$$\frac{3}{4}\frac{E\alpha T}{1 - \sigma} \cdot \frac{\lambda}{a}.$$

Since this is proportional to λ/a, it shows that localized heating does not produce large circumferential stresses. This is true, of course, only while there is no *axial* variation of temperature.

As to the axial stress under such conditions, the parts (i) and (ii) of Art. 8 are confined to the heated strip and occur throughout its length: (iii) and (iv) are distributions due to forces and moments localized on the ends of the heated strip. In the interior these will set up only very small stresses. In the interior, therefore, there will be an axial stress, given by $-\frac{1}{2}E\alpha T(1 \pm 2\zeta/h)$, confined to the heated strip, or a compressive stress varying from zero at the inside to $E\alpha T$ at the outside.

The stress at the ends of the cylinder presents a separate problem, and can be dealt with approximately by methods given in another paper (2). It may

---

* *This disregard of the restriction to smooth temperature variations, referred to in Art. 3, is of no more importance here than its equivalent in plane stress systems with discontinuous boundary stress. The discontinuity conveniently replaces a variation as abrupt as is allowed, without seriously affecting the conclusions.*

be shown that there would be local tensile circumferential stresses at the ends with a maximum value $2E\alpha T/(3 + \sigma)$.

14. The thermal stress in a *thick* cylinder with a steady-state temperature distribution due to surface temperatures arbitrarily distributed round the inside and outside surfaces, but independent of the axial co-ordinate, can be reduced, as was shown by N. Muschelišvili (5) and M. A. Biot (1), to an axial stress, and a dislocational stress corresponding to the stress specified above by means of X_o, Y_o and M_o. In order to find the appropriate magnitudes of the dislocations it is necessary first to obtain the solution of the potential problem of finding the temperature distribution from the surface temperatures.

By restricting the investigation described in this paper to the thin cylinder, the potential problem is avoided, and it becomes possible to find the stress and strain in terms of arbitrarily given surface temperatures for a cylinder of any shape and variable thickness. It should be said, however, that the potential problem presents no difficulties in the particular case of the uniform, thick circular cylinder. Explicit formulas for this case are given in another paper (3).

<div align="center">

References

</div>

1. Biot, M. A.   Phil. Mag. 19 : 540-549.   1935.
2. Goodier, J. N.   Physics, 7 : 156-159.   1936.
3. Goodier, J. N.   J. Applied Mechanics, March. 1937.
4. Kent, C. H.   Trans. Am. Soc. Engrs. 53 : 167-180.   1931.
5. Muschelišvili, N.   Bulletin de l'Université de Tiflis, 3.   1923.
6. Timoshenko, S. and Lessells, J. M.   Applied elasticity.   East Pittsburgh, Pa., Westinghouse Technical Night School Press.   1925.
7. Timoshenko, S.   Strength of materials.   Vol. II.   D. Van Nostrand Company, Inc. New York.   1930.
8. Timoshenko, S.   Theory of elasticity.   McGraw-Hill Book Company.   New York. 1934.

THE SPECIFIC HEAT OF COPPER FROM 30° TO 200° K.[1]

By S. M. Dockerty[2]

Abstract

An all-metal adiabatic vacuum calorimeter was used to determine the specific heat of copper over small temperature intervals from 30° to 200° K. The accuracy is considered to be within 0.05% for the greater part of the range. A curve is given showing the variation with temperature of the characteristic temperature, θ, for copper.

Introduction

Bronson, Chisholm, and Dockerty (2, 4) described the development of an all-metal adiabatic calorimeter and its use in precision measurements of the specific heat of copper from $-80°$ to $100°$ C. The present paper deals with the construction of a similar type of calorimeter for much lower temperatures, used to determine the specific heat of copper from 30° to 200° K.

The method, that of electrical heating under adiabatic conditions, has also been described (2, 4). The general features can be seen from the diagram of the apparatus in Fig. 1. The calorimeter is cooled down to the lowest
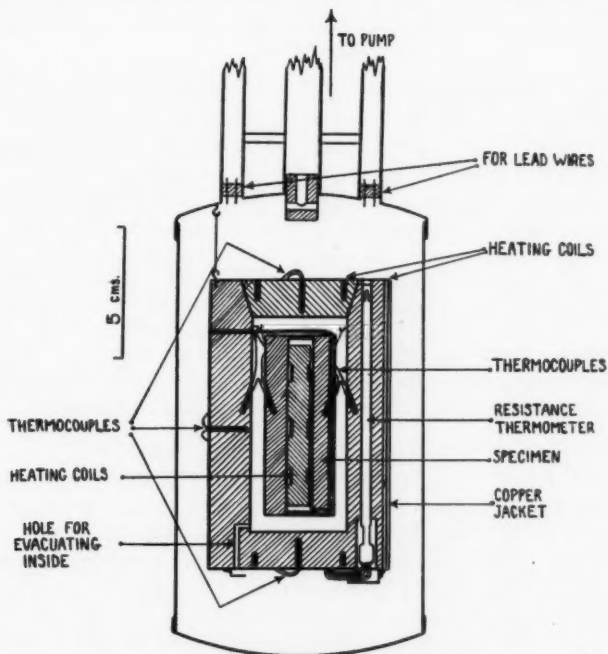

Fig. 1. *Adiabatic calorimeter.*

point of the range at which one wishes to work, by immersing the container in a low temperature bath, the rate of cooling being speeded up somewhat by having hydrogen gas in the container.

When the desired temperature is reached the container is evacuated. The specimen is heated so as to change its temperature in steps of 5° to 8°, the times of heating varying from 15 to 25 min. Adiabatic conditions are obtained by keeping the temperature of the jacket as nearly as possible equal to that of the specimen, as indicated by the differential thermocouples. The temperatures are so adjusted, before and after the heating period, that the differences between the jacket and the specimen are less than 0.001° C. Thus the temperature of the jacket, as measured by the resistance thermometers, will be also the temperature of the specimen. The electrical energy supplied was measured, to within 0.02%, with a potentiometer and a standard cell that was recently calibrated in the laboratories of the National Research Council of Canada. The mass of the specimen was known to within 0.01%. Temperature differences were measured to within 0.02% for the greater part of the range, the precision being somewhat less than this at low temperatures.

Apparatus

Jacket

Some difficulty was experienced with temperature gradients in the jacket of the older apparatus owing to the faulty distribution of heat loss. This was largely avoided in the present apparatus by using pure copper for the jacket, and by high evacuation which increased the thermal resistance between the jacket and the container about five times. Temperature gradients that were due to non-uniform heating were eliminated as before by winding separate heating coils on the sides and ends of the jacket; because of the high vacuum it was necessary to cement these coils in deep grooves.

Differential thermocouples between the sides and ends of the jacket, as shown in Fig. 1, served to indicate temperature inequalities over the inner surface. These were put in from the outside and were left in permanently, so that adjustments could be made during the actual experiments.

Two jackets were made by machining a 3-in. bar of copper. The first, which was used for most of the measurements above liquid air temperature, was about one and one-half times as large as that shown in Fig. 1, and differed from it in that it was divided horizontally at the centre into two symmetrical sections. This feature proved somewhat troublesome because it was found difficult to keep both sections at the same temperature. This equality was necessary because the resistance thermometers would indicate the temperature of the section in which their coils were situated. In addition, it was found that, because of the high vacuum, the size could be reduced considerably without affecting the accuracy of the results; this feature was desirable for the cooling to liquid hydrogen temperatures. A new jacket was therefore made as shown in Fig. 1. Care was taken to keep the end plug at the same temperature as the rest of the jacket, but a slight difference

would have no serious effect.   Small leads of copper wire were used to prevent the production of cold spots on the jackets at low temperatures where the thermal conductivity of copper becomes quite high.

Copper Specimen

This consisted of a bar of commercially pure cold-rolled copper, a copper plug, and an 80-ohm manganin heating coil fitted together as shown in Fig. 1. The weights of the specimens used with the large and small jackets were about 650 and 320 gm. respectively.   The amount of foreign material such as silk insulation, silk suspension, cement, and shellac was reduced to less than 0.1% of the total copper equivalent.

Because of the high vacuum it was necessary to bind the heating coil to the plug with a thin coat of shellac.   Small copper leads were used, and care was taken that these should be in good thermal contact with both the specimen and the jacket.

The two-junction copper-constantan thermocouples were cemented in small holes in the specimen and the jacket respectively as shown.   With a sensitive galvanometer these thermocouples would indicate temperature differences between the specimen and the jacket of less than 0.001° C.

Resistance Thermometers

Temperatures were measured with metal-stem resistance thermometers of platinum and lead placed in holes bored lengthwise in the jacket.   To prevent heating and lagging effects it was necessary that the thermometers should not be evacuated with the rest of the system.   They were therefore filled with helium gas at a pressure of one atmosphere, and sealed.   A very satisfactory type of seal, which holds at low temperatures, is shown in Fig. 2.

Resistances were measured with a carefully calibrated Müller bridge maintained at a constant temperature in a thermostatic box. Small copper wire leads were used and inequalities in compensation were balanced out by a method involving two readings on the bridge (7).

The platinum coil was made of 0.002 in. wire ($r_0 = 30$ ohms) obtained from Johnson-Matthey, with a specified value for δ (Equation (1)) of 1.49.   The lead coil was of 0.003 in. extruded wire ($r_0 = 9$ ohms) obtained from the Baker Chemical Company, and was rated of high purity.

The platinum thermometer was calibrated in ice, steam, liquid oxygen, liquid hydrogen, and liquid helium in the usual way.   The last two points proved to be of no interest from the point of view of calibration.   In addition, a careful calibration was made between $-183°$ C. and $-210°$ C. by means
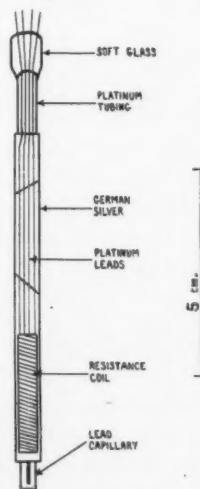
Fig. 2.
Resistance thermometer.

of an oxygen vapor pressure thermometer.   Pure gas was obtained for this purpose by heating potassium permanganate in a vacuum.

The values of the resistance ratio $\left(R = \dfrac{r}{r_0} \right)$ obtained for the various temperatures are given in Table I.   Repeated calibrations at some of these points showed no noticeable change over a period of a year.

TABLE I

RESISTANCE RATIO FOR PLATINUM THERMOMETER

Temp., °C.	R	Temp., °C.	R
100.00	1.38976	−191.01	0.21407
0.00	1.00000	−195.73	0.19377
−182.98	0.24891	−210.41	0.13152
−187.76	0.22823	−252.78	0.00957
−188.66	0.22434	−269.0	0.00438

The lead thermometer was calibrated in ice and in liquid hydrogen, and indirectly for the range −180° to −210° C. by comparison with the platinum thermometer during the actual experiments.   A slight zero shift was observed after the thermometer had been immersed in liquid air or in liquid hydrogen. The values of R obtained for the oxygen and hydrogen points were 0.29725 at −182.98° C. and 0.03615 at −252.78° C.

Resistance of Platinum.   The international Temperature Scale (3) is defined in terms of the platinum resistance thermometer by the equation,

$$ t - t_{pt} = \delta \left(\frac{t^2}{100^2} - \frac{t}{100} \right) + \gamma \, (t - 100) \, t^3 \; , \tag{1} $$

for $0° > t > -193°$ C.   However, it has been found by Heuse and Otto (10), and by Keesom and Dammers (11), that temperatures derived by means of Equation (1) depart from the thermodynamic scale by as much as 0.05° C. at −80° C. and −140° C., and in opposite directions.

Henning (9) has deduced that the resistances of different specimens of platinum should satisfy the relation,

$$ \Delta R = a(R - 1) + b(R - 1)^2 \; , \tag{2} $$

where R is the resistance ratio r/r_0.   Onnes (13) has shown that this relation holds to −215° C. with an accuracy in the derived temperatures of 0.02° C. Below this temperature no satisfactory relation has been found for comparing the resistances of different samples.

Temperatures were calculated directly by means of equation (1) from the resistance measurements of the platinum thermometer, and also by comparison with a detailed standard calibration by means of Equation (2).   The standards used were Henning's thermometer No. 29 to −195° C., and Onnes' No. 23′ from −195° to −210° C., the values of R for the standards being taken from

Leiden Comm. Supp. 58. Temperatures calculated by the two methods differed at some points by as much as 0.06° C. This gave rise to differences of as much as 0.1% in the temperature intervals. This is in agreement with the results of Heuse and Otto, and Keesom and Dammers. The method of comparison by Equation (2) was found to give close agreement with the calibration by means of the oxygen vapor pressure thermometer. The latter method was therefore adopted for the calculation of temperatures to −210° C.

Resistance of Lead. It has generally been found that the resistance ratios R, R', of different specimens of lead can be compared by means of the relation,

$$R' = \frac{R - a}{1 - a},$$

which reduces to

$$\Delta R = a(R - 1). \tag{3}$$

Temperatures were first calculated by means of Equation (3), using as a standard a specimen calibrated in detail by Onnes (5) and deriving the constant a from the resistance at the hydrogen point. This method gave only approximate agreement with the calibration points at higher temperatures, and consequently the same Equation (2) that was used for platinum was also adopted for lead, with the constants a and b determined from the hydrogen and oxygen points. A further small correction term was added to allow for a discrepancy of 0.04° at −210° C.

Experimental Measurements

To test the reliability of the calorimeter under widely different experimental conditions some determinations of the specific heat, with the copper specimen above room temperature, were made; *(A)* with the calorimeter in a water bath, and *(B)* in a bath of liquid air. With the large calorimeter the values obtained from *(B)* were 0.15% higher than those from *(A)*. In view of a similar correction in the previous investigation (4) it was thought that, with a liquid air bath, the correction would be proportional to the heat loss from the jacket. The measurements at temperatures above that of liquid air were made with this calorimeter. However, it was feared that at liquid hydrogen temperatures, where the heat capacity of copper is low, the above correction might have a larger value, and therefore the smaller calorimeter was constructed for use in the lower temperature region. Results obtained above room temperature with this new calorimeter for Cases *(A)* and *(B)* agreed within 0.02% of each other and within 0.05% of those obtained with the large calorimeter for Case *(A)*. It was found that, when the differential thermocouples were kept balanced, the temperature of the specimen did not change by more than 0.001° C. in one hour.

Measurements were made with the small calorimeter from 30° to 90° K. and two determinations were made at 93° K. and 133° K. At both these temperatures the results were 0.15% lower than those obtained with the large calorimeter. This showed that the correction factor did not vary as first supposed but was constant to 90° K.

Table II gives the values obtained for the specific heat of copper from 30° to 200° K. Temperatures are given in the Kelvin scale (0° C. = 273.15° K.). The value of C_p is given in joules per gram and in calories per mole (1 Cal.$_{15°}$ = 4.1835 electrical joules). The values of C_v are calculated from the relation

$$C_p - C_v = 1.60 \times 10^{-5} C_p^2 T .$$

The values of the characteristic temperature, θ, were found from a table of Debye functions given by Beattie (1). A value of 5.9613 calories per mole was used for $3R$.

Since some of the temperature intervals were as great as 8° C., calculations were made to find the difference between the mean specific heat over the range in question and the true specific heat at the mean temperature. For all except the two lowest points the difference proved to be within the limits of experimental error. For the first and second points however the correction amounted to about 1%. This correction was quite accurately determined by a graphical method.

TABLE II
THE SPECIFIC HEAT OF COPPER

Temp., °K.	C_p Joules per gm.	C_p Cal. per mole	$C_p - C_v$ Cal. per mole	C_v Cal. per mole	θ
28.64	0.02280	0.3475	0.0002	0.3473	314.0
35.93	0.04440	0.6745	0.0005	0.6740	310.5
42.58	0.06985	1.047	0.001	1.046	309.1
50.13	0.09855	1.497	0.002	1.495	309.5
59.24	0.1339	2.035	0.004	2.031	310.7
67.21	0.1620	2.462	0.007	2.455	312.7
74.64	0.1870	2.840	0.009	2.831	312.9
87.45	0.2239	3.402	0.016	3.386	313.0
87.88	0.2249	3.417	0.016	3.401	313.2
92.79	0.2365	3.594	0.019	3.575	313.8
93.18	0.2373	3.606	0.019	3.587	314.0
97.41	0.2463	3.743	0.022	3.721	314.9
103.08	0.2579	3.919	0.025	3.894	315.1
108.51	0.2681	4.074	0.029	4.045	315.3
113.73	0.2772	4.212	0.032	4.180	314.9
119.38	0.2861	4.347	0.036	4.311	314.9
125.42	0.2947	4.467	0.040	4.438	314.6
131.29	0.3025	4.597	0.044	4.553	313.9
132.97	0.3043	4.624	0.045	4.579	314.4
137.48	0.3092	4.699	0.049	4.650	314.8
144.24	0.3171	4.818	0.054	4.764	312.9
151.08	0.3236	4.917	0.058	4.859	312.3
157.79	0.3293	5.004	0.063	4.941	312.0
164.71	0.3345	5.083	0.068	5.015	312.0
171.83	0.3399	5.165	0.073	5.092	310.4
178.84	0.3443	5.232	0.078	5.154	309.9
186.33	0.3486	5.297	0.084	5.213	309.6
194.29	0.3528	5.361	0.089	5.272	308.6

Discussion of Results

The accuracy of the results is limited in general by that of the temperature measurements. Above 80° K. it is considered to be within 0.05%. Below this temperature the accuracy is somewhat reduced because of uncertainties in the use of the lead thermometer. An error of more than 0.01° in a 5° interval in this range is considered unlikely.

Fig. 3 gives the values of θ plotted against the temperature. The corresponding values for the specific heat can be found from Beattie's table. Above 90° K. only one point lies off the curve by an amount corresponding to more than 0.05% in C_p. The rise in the curve at 70° K. corresponds to about 0.3% in C_p and is thought to be well within the limits of error. The existence
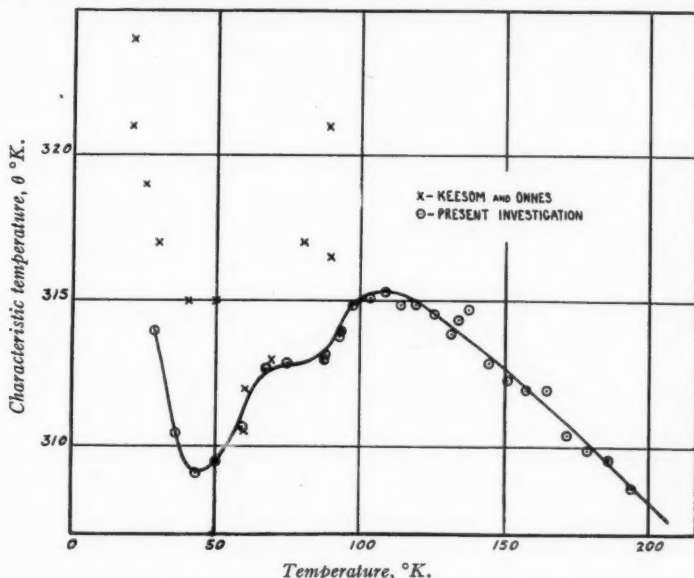
FIG. 3. *Characteristic temperature, θ, for copper.*

of a minimum at about 50° K. is in fair agreement with the work of Keesom and Onnes (12). Their points show a maximum deviation from the present curve of about 3%, which was the accuracy they had claimed. Both show an increase in the value of θ at lower temperatures.

Above 110° K. the curve falls quite rapidly. In the previous work above 200° K. it was found that the specific heat curve could be fitted with a constant value of θ if a term, linear with the temperature, were added to Debye's equation. This equation was found to hold, in the present case, to 100° K. with an accuracy of 1%. Below this temperature however the equation failed, since it amounted roughly to a linear correction in θ.

The results agree with those of Griffiths and Griffiths (8) at room temperature but fall below their curve by 4% at 140° K. The results agree however at this temperature with the results of Eucken and Werth (6).

In the previous work (2, 4) differences of 0.2% were found in the specific heat of specimens of specific gravities 8.8 and 8.9. The specific gravity of the specimen used in the previous work from −78° to 0° C. was 8.90, while that of the specimen used in the present work was 8.91. The two should have specific heats very nearly equal. Later unpublished work has shown

that the values previously obtained (4) are too low by 0.2%. When this correction is made the two agree to within 0.05%, both at room temperature and at 200° K.

Acknowledgments

The author wishes to express his indebtedness to Dr. E. F. Burton for his supervision and interest in this work, and to Mr. J. O. Wilhelm for valuable advice and assistance with the low temperature technique.

References

1. BEATTIE, J. A.   J. Math. Phys. 6 : 1-32.   1926.
2. BRONSON, H. L., CHISHOLM, H. M. and DOCKERTY, S. M.   Can. J. Research, 8 : 282-303. 1933.
3. BURGESS, G. K.   Bur. Standards J. Research, 1 : 635-640.   1928.
4. DOCKERTY, S. M.   Can. J. Research, 9 : 84-93.   1933.
5. EUCKEN, A.   Handbuch. der Experimentalphysik. VIII, 1 : 64.   Akademische Verlagsgesellschaft m.b.H., Leipzig.   1929.
6. EUCKEN, A. and WERTH, H.   Z. anorg. Chem. 188 : 152-172.   1930.
7. GLAZEBROOK, SIR RICHARD.   Dictionary of applied physics; Resistance thermometry. Vol. 1.   Macmillan and Company, Ltd.   London.
8. GRIFFITHS, E. H. and GRIFFITHS, E.   Trans. Roy. Soc. London, A, 214 : 319-357.   1914.
9. HENNING, F.   Ann. Physik, 40 : 635-667.   1913.
10. HEUSE, W. and OTTO, J.   Ann. Physik, 9 : 486-504.   1931.
11. KEESOM, W. H. and DAMMERS, B. G.   Physica, 2 : 1080-1090.   1935.
12. KEESOM, W. H. and ONNES, H. K.   Proc. Acad. Sci. Amsterdam, 18 : 484-493.   1916.
13. LEIDEN COMMUNICATION SUPPLEMENT 58.   1926.

STUDIES OF CARBON BLACK

III. THE CHANNEL PROCESS—PRODUCTION FROM PYROLYSIS WASTE GASES[1]

BY L. M. PIDGEON[2]

Abstract

The waste gases obtained during the pyrolysis, in baffled metal tubes, of 70:30 propane-butane mixtures at temperatures between 800° and 850° C., with the object of producing liquid aromatics, have been used to produce carbon black in an experimental channel plant. The hydrocarbon mixture if utilized directly to produce carbon black yielded up to 4.9 lb. per 1,000 cu. ft. When the mixture was subjected to pyrolysis about 33 lb. of liquids (23 lb. in the gasoline range) was produced, while the off-gas yielded 5.4 lb. of carbon black. Yields of carbon black up to 10 lb. per 1000 cu. ft. were obtained with lower yields of liquid. Experiments on synthetic gas mixtures showed that the olefines were largely responsible for the production of carbon black from the pyrolysis off-gas. A large number of tests on rubber indicated that the carbon reinforces rubber in a manner as good as or better than that of the commercial gas blacks at present used in the rubber industry.

Introduction

The channel process, which is employed almost exclusively in the production from natural gas of the carbon black used largely in the rubber industry, is so wasteful that it fails to recover more than a small fraction of the carbon present in the gas. The carbon black industry depends, therefore, on the existence of enormous amounts of hydrocarbon gases for which no other use can be found and which otherwise would be wasted after removal of the natural gasoline. So large, however, have been the amounts of gas available for carbon black production that supply has exceeded demand in recent years, a condition that has been responsible for the low price to which carbon black has fallen. In these circumstances it may be readily understood that little incentive has been offered to improve the methods of production. This situation, while it will undoubtedly continue for some time, cannot be regarded as a permanent one, and indications of a change are already in view. Eventually more economical methods of production must be evolved, or the price of carbon black will increase, and a readjustment of the relative position of this filler in the rubber industry must take place.

Thermal process methods have achieved notable improvements in the carbon recovery but, to date, they have been unable to duplicate the quality of channel blacks and have, therefore, enjoyed but limited application. It seems that initial attempts to improve the methods of production might well

take the form of more efficient utilization of the gas supplies on hand, by the use of the established flame impingement process.

In the experiments to be described it has been found that the off-gas from low-pressure pyrolysis carried out on propane and similar gases in the Cambron Bayley apparatus*, with the object of securing liquids (mostly aromatic) as the primary product, is eminently suitable for the production of carbon black by the channel process.   In fact, the amount of black that may be produced from a given volume of stabilizer gas is considerably greater if the gas is first caused by pyrolysis to yield aromatic liquids and the off-gas is then burned, than if the stabilizer gas is burned directly.

The gases that have been employed in these experiments were produced during the pyrolysis of a mixture of propane and butane, this particular mixture being employed because of its similarity to stabilizer gas of which large amounts are available in various parts of the world.   The pyrolysis of these gases was carried out by Cambron and Bayley, who have described the experimental details (1, 2, 3, 4).   The hydrocarbon mixture was passed through metal tubes at temperatures up to 850° C., the tubes being equipped with a special system of baffles designed to produce turbulent flow and thereby assist the process of heat exchange.   These authors placed the off-gas at the disposal of the writer.

The composition of the gas obtained from the pyrolysis of a hydrocarbon mixture depends on the conditions of operation.   The initial step in pyrolysis is the formation of olefines, while further heating results in the "polymerization" of these gases to aromatics and other hydrocarbons, depending on the temperature and pressure at which the operation is carried out.   The highest yields of carbon black would be expected from the off-gas when its olefine content is a maximum, since it is well known that gases containing large amounts of "illuminants" are prolific producers of carbon in free flames.   The conversion of olefines to aromatics involves an increase in the percentage of methane and hydrogen and a reduction in the carbon content of the off-gas, which consequently reduces the yield of carbon black which may be obtained. It has been noticed, however, that the ethylene concentration does not fall below a certain value unless the pressure at which the pyrolysis operation is carried out is materially increased.   When the time of contact in the pyrolysis process is lengthened and the yield of aromatics thus increased, a larger volume of off-gas is produced.   This gas expansion may be such that, despite the fact that the off-gas is "leaner", the total yield of carbon black is not seriously reduced.

The effect on the yield of carbon black of varying the gas composition has been examined both by altering the conditions in the pyrolysis, so as to produce off-gas of various compositions, and by the use of synthetic mixtures. In order to ascertain the relative efficiency of the joint pyrolysis-channel process, a number of determinations have also been made on the possibilities of carbon black production from the original propane-butane mixture, without preliminary treatment in the pyrolysis apparatus.

---

* *U.S. Patents 2,002,524 and 2,002,525; also patents elsewhere.   Cf. references 1–4.*

Experimental

PRODUCTION OF CARBON BLACK

Apparatus and Method

The production of carbon black was carried out in the experimental channel plant which has been described in detail (11). The 6 in. channel employed in the previous experiments was replaced by an 8 in. channel, but otherwise the conditions were identical with those already described.

The gases passed from the charcoal absorbers of the pyrolysis apparatus to a gasholder of 4 cu. ft. capacity, and thence to the channel plant. The conditions of operation of the pyrolysis apparatus were similar to those of Cambron and Bayley's experiments Nos. 65–69 (4), with the exception that a 70:30 propane-butane mixture was employed in place of propane. This substitution resulted in a slight enrichment of the off-gas, chiefly represented by higher olefine concentrations, but did not change the general relations in any way.

It has been indicated (11) that when the gas composition, the gas pressure, and the burner tip have been specified in a given experimental apparatus, the important remaining variables are channel height and draft control. Many other factors exist that might presumably influence the results, but experience has shown that they exert only a small effect, although quantitative information on the subject is not available. Attention has, therefore, been confined to the effect of channel height, draft control, and gas composition on the yield and characteristics of the carbon black.

Effect of Channel Height

The effect of channel height has been examined by the use of a very rich gas that happened to be available in large quantities during a life test performed on the metal tubes of the pyrolysis furnace. No liquids were formed during the pyrolysis, so that this gas is a suitable one for the recovery of the

TABLE I

EFFECT OF CHANNEL HEIGHT ON YIELD

	A Carbon collected from walls and channels				B Carbon from channels					
Experiment	C11	C10	C12	C13	C29	C16	C17	C18	C19	C21
Channel height, in.	1.84	2.24	2.56	3.24	1.92	2.94	2.44	2.84	3.20	3.61
Yield, lb. per 1000 cu. ft.	4.2	4.7	4.8	4.6	3.3	4.1	4.4	3.9	3.4	2.2
Yield based on propane-butane pyrolyzed	8.4	9.4	9.6	9.2	6.6	8.2	8.8	7.8	6.8	4.4

Gas composition: C_2H_4, *24.0;* C_3H_6, *12.3;* C_2H_2, *1.3;* H_2, *14.8%; paraffin residue, 47.6%.*
Expansion, 100%.
Burner: Cabot type, 0.022 in. slot. Gas rate, 6 cu. ft. per hr. Drafts, 28%.

ii ximum amount of carbon black. The results are shown in Table I and plotted in Fig. 1. For a given channel height, a sharp maximum is obtained, the position of which depends on the particular tip and gas pressure chosen.

The yields obtainable from this gas are at least three times as great as those produced from methane. They also represent a considerably higher percentage of the theoretical recovery of the carbon, as will be seen presently.
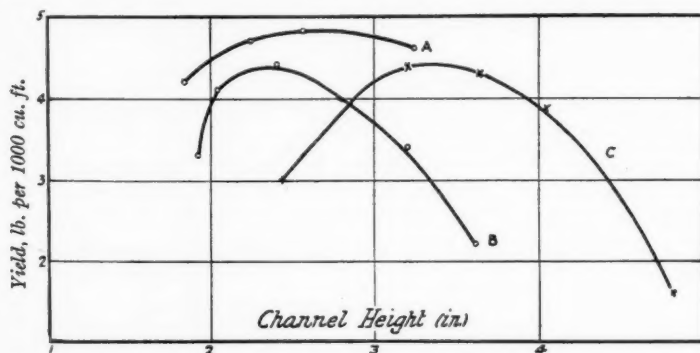
FIG. 1. *Effect of channel distance on yield (0.022 in. Cabot tip). A. Pyrolysis off-gas, all carbon in burner chamber recovered. B. Pyrolysis off-gas, carbon from channels only. C. Propane-butane, carbon from channels only.*

Table II shows the yields obtained with the original propane-butane mixture. Again a fairly sharp maximum channel setting is required to obtain the optimum yield. In the yields obtained from the rich waste gas, to determine the actual recovery from the propane-butane pyrolyzed, the yield from

TABLE II

EFFECT OF CHANNEL HEIGHT ON YIELD

	A Burner: Cabot type, 0.022 in. slot Gas rate, 3.4 cu. ft. per hr. Drafts, 28%						B Burner: Cabot type, 0.012 in. slot Gas rate, 2.22 cu. ft. per hr. Drafts, 28%						
Experiment	C31	C32	C33	C34	C45	C46	C35	C36	C37	C38	C41	C39	C40
Channel height, in.	2.44	2.84	3.20	3.64	4.04	4.84	1.24	1.64	2.04	2.44	2.84	3.24	3.64
Yield, lb. per 1000 cu. ft.	3.0	3.9	4.4	4.3	3.9	1.8	2.3	2.8	3.6	4.9	3.8	2.2	1.1

Gas composition: C_3H_6, 70; C_4H_8, 30%.

the waste gas must be multiplied by the expansion taking place during pyrolysis, which in this case was the factor 2. This procedure has been followed in Table I, where values as high as 9 lb. per 1000 cu. ft. are given. Thus the total yield in the joint process is considerably greater than that when the paraffins are utilized directly.

It is also evident from Table I (*A* and *B*) that, under these experimental conditions, much larger amounts of carbon are liberated from the flame than are retained on the channel. Carbon was deposited on the walls and flues of the apparatus, while considerable quantities were lost into the air. When all the carbon in the apparatus was collected, the apparent yield was much greater, as is shown in Table I, *A*, and the effect of channel height was much less pronounced, as might be expected.

Considerable doubt has been expressed as to the quality of the carbon which escapes from the flame without being deposited on the channel (12), since its genesis is similar to that of lampblack, a material that is inferior to carbon black as a reinforcing agent for rubber. In computing the yields and in subsequent tests, only carbon deposited on the channel has been considered. It would be necessary to employ a much larger depositing area than is customary in the case of natural gases composed largely of methane, if gases that burn with very smoky flames were used in full-scale practice. The same effect could be produced with smaller flames, although changes in flame dimension cannot be made without consideration of the type of carbon that it is desired to produce. The use of smaller tips increased the yield obtainable with propane-butane as shown in Table II, *B*, while with the same pyrolysis waste gas as employed in the experiments of Table I even more noticeable gains were achieved by the use of smaller burners. Thus, with a 0.012 in. tip burning gas at the rate of 3 cu. ft. per hr. the yield rose to 5.7 lb. per 1000 cu. ft., which is an improvement of 25% over the best yield given in Table I,*B*, while the amount of carbon deposited on the walls was correspondingly reduced, an effect undoubtedly desirable where continuous operations are involved, as otherwise the outlets would require constant cleaning.

Effect of Draft Control

In the previous experiments (11) in which methane was examined, it was found that when the flames burned steadily, without flicker or pulsation, no change in yield was brought about by restriction of draft, until the limit tolerated by the flames was reached, at which point the yield was seriously reduced. On the other hand, when the convection currents set up were such as to cause disturbance of the flames when the draft was unrestricted, it was found that the yield was unfavorably affected, and improvement could be achieved by restriction of draft.

A similar behavior has been observed in the present case. The results of experiments in which the same gas as that indicated in Table I was used are shown in Table III. The flames flickered badly with unrestricted draft and the yield was adversely affected. Improvement in the burning of the flames was accompanied by increase of yield as the draft was restricted, until the limit of tolerance was attained, at which point the luminosity of the flames was impaired with consequent reduction in yield. These results are in agreement with those previously given (11) and also with the opinions of Francis (7), who has indicated that theoretically no improvement in yield can follow dilution with nitrogen or carbon dioxide of the air surrounding the hydrocarbon flame.

TABLE III
Effect of draft control

Experiment	C22	C23	C24	C18	C25
Yield, lb. per 1000 cu. ft.	3.1	3.2	3.5	3.9	3.5
Draft aperture, %	100.0	50.0	38.0	28.0	21.0
Flue gas composition, %					
Carbon dioxide	1.0	1.5	1.8	3.8	3.5
Oxygen	19.2	17.2	16.3	14.5	14.1
Residue	79.8	81.3	81.9	81.7	82.4

Burner: Cabot type, 0.022 in. slot.   Gas rate, 6 cu. ft. per hr.   Channel height, 2.84 in.

The flue gas analyses bear no relation to those determined previously for methane (11), and show again the futility of attempting to specify draft conditions in any manner that may have general application.

As pointed out previously (11), the effect of draft control will depend on the channel height, and in exceptional circumstances very marked effects might be observed. Owing to the fact that a hydrocarbon flame becomes taller when the supply of air is restricted, the relative height of the depositing surface is altered. Thus if the channel had been set just above the flames, the recovery of carbon would be zero, while, by suitable reduction of draft, the flame might be lengthened to reach the channel upon which some carbon would then be deposited. In such circumstances draft control would obviously exert a very marked effect on the yield. The case is exceptional and in ordinary use it seems clear that the chief effect of draft control is to steady the flames.

Effect of Gas Composition

Clearly, in view of the present price of carbon black, it would not be commercially feasible to subject paraffin hydrocarbon gas to pyrolysis prior to burning it for carbon black production, if carbon black is the sole product made. If, however, pyrolysis is conducted in such a way as to yield substantially a maximum or optimum amount of aromatics, and these are collected and utilized as a source of motor fuel (of high octane rating), styrene, naphthalene, etc. (4), and the off-gas, containing olefines well suited to the production of carbon black in good yield, is then used for carbon black production, there are prospects of commercially successful operation. With this in mind a series of experiments was carried out in which the pyrolysis of a 70:30 propane-butane mixture (representing stabilizer gas) was conducted under conditions designed to yield various amounts of aromatics, and the off-gas was burned to yield carbon black by the channel process. The results are given in Table IV.

The yield of carbon black based on the off-gas decreases in a fairly regular manner as the amount of liquid products obtained during the pyrolysis increases. When, however, this yield is based on the amount of gas entering

TABLE IV

RELATION BETWEEN COMPOSITION OF OFF-GAS AND YIELD OF CARBON BLACK

Experiment	B6	B25	B12	B16	B30
Pyrolysis					
Temperature	810(s)	830(s)	810	830	850
Liquids (1 hr.), gm.	—	41.6	53.2	76.0	101.5
Expansion, %	73	99	101	103	117
Off-gas composition					
C_2H_2	0.9	0.9	1.0	0.9	1.1
C_2H_4	24.6	26.6	26.7	28.0	25.9
C_3H_6	12.0	9.5	7.5	4.3	3.1
H_2	16.3	16.7	16.6	17.7	19.7
Residue	46.2	46.3	48.2	49.1	50.2
n, Residue (C_nH_{2n+2})	1.4	1.2	1.1	1.1	1.0
Carbon black production					
Yield from off-gas, lb. per 1000 cu. ft.	3.9	3.5	3.4	2.7	2.5
Yield based on original propane-butane volume	6.6	6.9	6.8	5.5	5.4
Theoretical recovery based on off-gas, %	7.6	8.2	8.4	7.1	7.2
Theoretical recovery based on original propane-butane, %	5.9	6.2	6.1	4.9	4.8

(s)—*Shorter furnace, 85 cm.*

the pyrolysis apparatus, the results are somewhat different. In B6, for example, the amount of cracking was incomplete, as shown by the high propylene content and the high carbon number of the residue; hence the expansion was not great and the total yield of carbon black was less than that in B25, in which, with a lower olefine content and lower yield based on off-gas, the greater expansion has resulted in a larger over-all yield. Even when the maximum amounts of liquids are being synthesized in the pyrolysis operation, the total yield remains at a reasonable value. Thus, comparing the results of B30 and B12, the yield of liquids has been increased by 100%, while the total yield of carbon black has suffered a loss of but 18%. This phenomenon is due to the fact that in these pyrolysis experiments the percentage of ethylene remained substantially constant, even with very different yields of liquid. The increase of liquids has taken place at the expense of the amount of propylene, which decreases to less than one-half of the amount present when the yield of liquids is low.

The conditions most suitable for the production of useful aromatics are typified by Experiment B16, since, at the temperature and time of contact in question, the ratio of light oil to tar in the recovered liquids is most favorable.

The important feature of the process is the production of useful aromatic liquids in good yields without, at the same time, reducing the amount of carbon black that may be recovered from the gas. In fact the amounts of carbon black that were produced from a given volume of stabilizer gas when first pyrolyzed and burned to produce carbon black were larger than when the gas was burned directly to form carbon. Thus, the best yield obtained with the untreated paraffin mixture was 4.9 lb. per 1000 cu. ft., while the same gas, after treatment in the pyrolysis plant produced 5.4 lb. per 1000 cu. ft., and some 23 to 25 lb. of light oil per 1000 cu. ft. would be recovered during the pyrolysis. For details of the composition of this oil and of the additional 10 lb. of tar which is obtained concurrently, reference should be made to the work of Cambron and Bayley (4).

Examination of Synthetic Mixtures

Hydrogen, ethylene, and methane constitute 95% of the off-gases. These gases have been mixed in various proportions in order that a search might be made for the important factors influencing carbon yield. To reduce the number of experiments, the channel and draft settings have been kept constant. This procedure introduces some error, since the optimum conditions for a given flame may not be the same as for another. The difference, however, is unlikely to be large when flames of similar type are used.

As shown in Table V, the yield obtained from either ethylene or methane is reduced by any addition of hydrogen. There is considerable difference in the relative sensitivity of various gases to this treatment. This is clearly shown in Fig. 2, in which the yields of various dilutions with hydrogen have been plotted as a percentage of the yield obtained with the pure hydrocarbon. In the case of methane the yield is sharply reduced by small additions of hydrogen; ethylene, on the other hand, is

TABLE V

EFFECT ON YIELD OF DILUTION WITH HYDROGEN

A. Methane

CH_4	H_2	Yield, lb. per 1000 cu. ft.	Per cent of original yield
100	0	1.2	100
95	5	1.1	92
90	10	0.8	66

B. Ethylene

C_2H_4	H_2		
100	0	4.3	100
95	5	4.2	98
90	10	4.1	95
85	15	3.4	79
75	25	2.2	51

C. 25% Ethylene and methane

C_2H_4	CH_4	H_2		
25	75	0	2.2	100
25	65	10	2.2	100
25	60	15	2.1	96
25	55	20	1.9	86
25	50	25	1.8	82

Burner: Cabot type, 0.012 in. slot. Gas rate, 2.7 cu. ft. per hr. Drafts, 21%.

much less affected; while replacement of methane by hydrogen in a mixture of methane and ethylene may be carried to considerable lengths before appreciable reduction in yield takes place. This fact is of importance in the
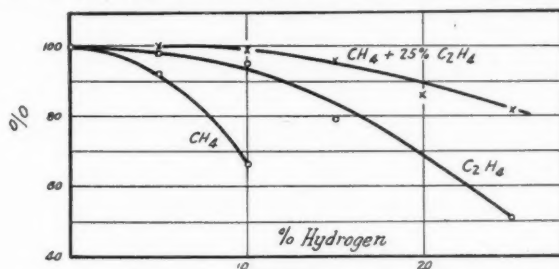

FIG. 2.   *Effect on yield of addition of hydrogen to various gases.*

production of carbon from pyrolysis off-gas, as increase in the yield of aromatics by pyrolysis tends to increase the proportion of hydrogen in the off-gas. In mixtures of this type the major portion of the carbon is supplied by the olefines, and, as long as the diluent gas is inflammable so that its presence does not seriously reduce the flame temperature, considerable amounts of the latter may be present before the yield is appreciably reduced. An example of this phenomenon is found in some results of Wiegand (14), who reported yields similar to those obtained with methane (1.0 to 1.3 lb. per 1000 cu. ft.), using a gas of the following composition:— H_2, 36.0; CO, 26.4; CH_4, 16.4; CO_2 and N_2, 13.2; illuminants, 7.2; O_2, 0.8%. With such a gas almost the whole recovery of carbon black must be due to the olefines.

The value of ethylene as a source of carbon black is further shown by the data in Table VI, where it can be seen that the yield varies with the amount of olefine added.

TABLE VI

EFFECT OF ADDITION OF ETHYLENE

Methane

CH_4	C_2H_4	Yield, lb. per 1000 cu. ft.
100	0	1.2
95	5	1.4
90	10	1.7
75	25	2.2
60	40	2.7

10% Hydrogen and methane

H_2	CH_4	C_2H_4	
10	90	0	0.8
10	85	5	1.3
10	80	10	1.6
10	65	25	2.2

A general summary of these results and those obtained with pyrolysis off-gas is given in Table VII. The higher yields obtained with the off-gas is due entirely to the presence of propylene as shown in Fig. 3. Extrapolation of the curve relating yield to propylene concentration gives a yield (2.0 lb. per 1000 cu. ft.) almost identical with that obtainable with synthetic mixtures containing the same ethylene concentrations. Hence, from these values it is possible to forecast, with a reasonable degree of certainty, the yields that would be obtained from any given mixture of gases.
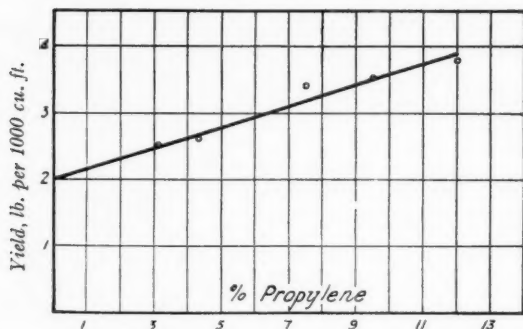
Yield, lb. per 1000 cu. ft.

% Propylene

FIG. 3. *Relation between propylene concentration in pyrolysis waste gas and carbon black recovery.*

TABLE VII

RELATION BETWEEN GAS COMPOSITION AND YIELD OF CARBON BLACK

	Pyrolysis off-gas					Synthetic gas	
C_2H_2	0.9	0.9	1.0	0.9	1.1	0.0	0.0
C_2H_4	24.6	26.6	26.7	28.0	25.9	25.0	25.0
C_3H_6	12.0	9.5	7.5	4.3	3.1	0.0	0.0
H_2	16.3	16.7	16.6	17.7	19.7	10.0	20.0
Residue	46.3	46.3	48.2	49.1	50.9	65.0	55.0
Yield, lb. per 1000 cu ft.	3.8	3.5	3.4	2.7	2.5	2.1	1.9

PHYSICAL PROPERTIES OF CARBON BLACK FROM PYROLYSIS WASTE GASES

Owing to the lack of a test capable of satisfactorily evaluating the properties of a carbon black designed for use in rubber, it is necessary to compare the new samples with standard commercial samples such as are in common use in the rubber industry. In appearance the experimental blacks had all the characteristics of typical channel blacks, showing the same intense black and high tinting strength. Grit was practically absent and the ash content was very nearly zero, owing to the smooth face of the depositing surface and the efficiency of the scrapers. The samples could be brushed through the finest screen without any residue being left.

The sorption of methylene blue was examined under experimental conditions similar to those described previously (10). The value for a sample obtained under conditions productive of maximum yield is shown in Table VIII, together with values obtained with commercial blacks under similar conditions.

TABLE VIII

SORPTION OF METHYLENE BLUE*

Sample	Mg. per gm. of carbon
Pyrolysis off-gas	37.6
Standard rubber black *B*	33.6
Standard rubber black *A*	32.0

* 0.25 gm. black shaken for one hour with 50 cc. of 0.25% aqueous methylene blue solution.

The carbon obtained from the pyrolysis off-gas showed slightly greater sorptive capacity under this test, but, as will be shown presently, the rate of vulcanization was actually more rapid than that with the commercial sample.

Reinforcement of Rubber

A preliminary examination was made by the use of the D.P.G. test formula, which has been described by the writer (11). The tensile properties of a sample produced from pyrolysis waste gas under conditions of maximum yield are shown in Table IX. The particular commercial sample, which was examined under identical conditions, gave somewhat lower values as shown.

TABLE IX
RUBBER REINFORCEMENT BY CARBON BLACK

Cure time, min.	200 %	300 %	400 %	500 %	T_b	E_b, %	Hardness (Shore)
C18							
65	35.5	70.4	111	181	220	565	57
85	52.1	101	162	237	282	560	64
105	56.6	106	174	252	287	555	64
125	63.2	111	179	257	282	530	64
Standard rubber black—Manufacturer "A"							
65	28.7	58.2	98.6	153.4	233	630	56
85	37.4	73.7	123.0	188	270	610	59
105	40.8	79.1	131.4	196	279	618	61
125	47.1	87.3	142.6	211	278	590	63

	Abrasion loss, cc. per hp-hr.
C18 *	151
Standard Rubber Black "A" *	161

*Cure time 95% of the optimum as shown by tensile tests. Stress, kg. per sq. cm.

Results of abrasion tests, obtained with the du Pont abrader by the use of the procedure recommended by the makers of this apparatus, are given in Table IX. The new black is slightly superior to this particular commercial sample.

Effect of Loading on Tensile Properties

Wiegand (14) has emphasized the importance in the evaluation of reinforcing agents of the energy or "proof resilience", which is essentially the work done in stretching the sample to the breaking point. When the energy for different pigment loadings is compared with that of the base mix, it is possible to obtain a curve that is representative of reinforcement and that exhibits a characteristic shape for any given filler. Wiegand suggests the

name "delta A" (ΔA) for this function, which is simply the double integral of tensile strength with respect to the elongation and percentage of pigment in excess of the base mix.

The evaluation of the ΔA function is likely to afford a clearer picture of the relative reinforcing properties of two pigments than that obtainable from a single determination using the same loading and accelerator.

To obtain results that will be comparative, it is necessary to choose an accelerator the effectiveness of which is relatively independent of the concentration of pigment. If this precaution is neglected, the results will be meaningless, and, as pointed out by Cranor and Braendle (5), attempts to adjust the differences in cure time by changing the concentration of accelerator will result in the introduction of enormous errors. These authors employed a heavily loaded litharge mix which was found to be nearly independent of the pigment concentration. In the present investigation the accelerator, Captax (mercaptobenzo-thiazole) was found to be satisfactory, since only small differences in rate of cure were noted with various concentrations of carbon black. The following formula has, therefore, been employed: Smoked sheet, 100; zinc oxide, 5; stearic acid, 4; Agerite resin, 1; Captax, 1; sulphur, 3; Genasco, 5.

Carbon black was added to the various mixes in the following proportions by weight (rubber 100), viz., 15, 35, 55, 75, and 100. The accelerator was added from a master batch and the sulphur was added last to the mix in order to reduce the danger of scorching, and also in deference to a suggestion appearing in the literature (9) that flocculation of the carbon may take place around the sulphur particles when they are present during the addition of the carbon. Vulcanization and testing were carried out as described previously, cures being made at 274° F. for 30, 45, 60 and 75 min. respectively.

The tensile results obtained in these experiments are shown in Table X and in Figs. 4 and 5, where the ultimate tensile strengths have been plotted against the time of cure. It is evident that this accelerator is relatively independent of the concentration of the carbon. At low loadings a slight retardation of cure is observed, while at the highest loadings a slight acceleration appears, although the curves at these concentrations are very flat. These differences are in the same direction as, but much smaller than, those observed by Goodwin and Park (8), using this accelerator with commercial blacks.

The behavior of the new carbon black in rubber is almost identical with that of the standard commercial sample, such differences as appear being no greater than would be found between two commercial samples obtained from different producers. The most noticeable difference is the greater stiffness that is imparted by a given concentration of the new black. This excessive stiffness proves to be detrimental at the highest loadings as the ultimate elongation and tensile strength are reduced. On the other hand, the new black will give the same stiffness and tensile strength at lower carbon loadings.

TABLE X

TENSILE PROPERTIES AT VARIOUS LOADINGS

Cure, min. at 274° F.	Carbon black from pyrolysis off-gas					Standard carbon black *B*				
	300 %	500 %	T_b	E_b, %	Hard-ness (Shore)	300 %	500 %	T_b	E_b, %	Hard-ness (Shore)
Base stock										
30	17.2	51.0	215	740	40					
45	20.6	60.0	228	718	42					
60	22.5	67.2	241	683	43					
75	22.5	67.6	222	690	44					
15 parts carbon										
30	21.9	64.8	196	740	44	19.9	62.4	173	715	43
45	27.7	82.1	240	737	47	27.2	84.1	224	703	47
60	33.8	100	272	738	49	32.1	100	252	697	49
75	37.5	109	277	720	51	36.1	110	283	713	50
35 parts carbon										
30	41.3	110	188	655	54	33.6	94.7	162	648	51
45	58.8	147	274	705	58	49.4	134	264	713	56
60	68.5	170	288	676	61	62.6	162	284	680	59
75	73.7	178	285	665	63	66.0	172	279	663	61
55 parts carbon										
30	73.4	162	208	598	63	59.6	141	190	603	66
45	97.6	205	251	591	69	84.1	189	265	645	68
60	112	231	270	588	71	100	218	280	613	70
75	124	246	272	553	73	110	234	284	598	71
75 parts carbon										
30	135	222	229	500	76	101	201	215	540	70
45	161	–	248	480	81	136	238	251	535	76
65	182	–	248	428	82	153	253	255	503	79
75	195	–	247	395	83	161	–	259	478	81
100 parts carbon										
30	192	–	215	350	84	171	–	211	410	84
45	216	–	216	300	88	194	–	226	383	86
65	–	–	220	265	90	218	–	239	345	87
75	–	–	217	238	90	224	–	236	328	90

Stress, kg. per sq. cm.   (Hardness—Shore "Durometer")

Smoked sheet, 100; zinc oxide, 5; stearic acid, 4; Agerite resin, 1; Captax, 1; sulphur, 3; Genasco, 5.
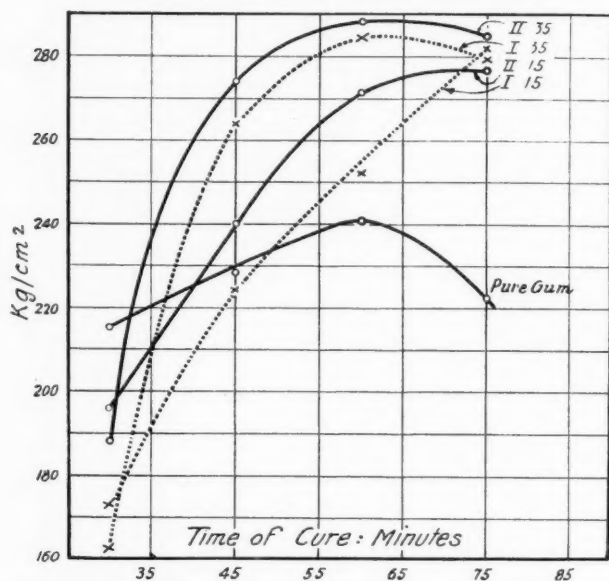
FIG. 4.   *Ultimate tensile strength at various cure times.   I. Standard rubber black B.
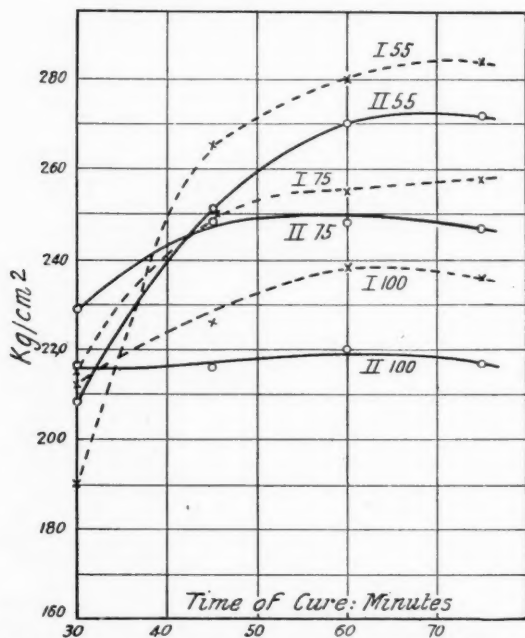II. Carbon black from pyrolysis off-gas.*

FIG. 5.   *Tensile properties at various cure times.   I. Standard rubber black B.   II. Carbon
black from pyrolysis off-gas.*

Delta-A Function

The stress-strain curves corresponding to the results of Table X were plotted and the areas under the curves obtained by means of a planimeter. These values, which correspond to the energy required to break the samples, are plotted against the concentration of carbon black in Fig. 6. Further
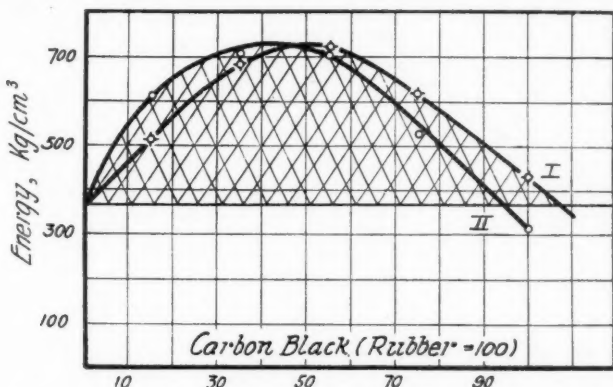

FIG. 6. *Energy-concentration relation. I. Standard rubber black B. II. Carbon black from pyrolysis off-gas.*

evidence of the fundamental identity of these two carbons is shown by the fact that the maximum energy values reached in each case is almost exactly the same, and that although the position of this maximum does not coincide, the actual magnitudes of the ΔA function (the shaded area in Fig. 6) are identical within the experimental error of determination. Thus the tensile properties of the new blacks are very similar to those of this commercial black. The blacks would legitimately be expected to behave in a similar manner in all the uses to which channel blacks are put.

Abrasion Resistance

Abrasion tests have been carried out on these samples with the du Pont Abrader (Table XI). It appears that the two blacks under test again show agreement within the experimental error.

It is of interest to note that the base mix was more difficult to abrade than the samples with low carbon black loadings. This phenomenon has

TABLE XI

ABRASION RESISTANCE

Sample	Loading	Specific gravity	Volume loss, cc. per h.p-hr.
Base mix	—	0.980	183
Pyrolysis off-gas	15	1.030	258
Standard rubber black "B"	15	1.029	245
Pyrolysis off-gas	35	1.093	232
Standard rubber black "B"	35	1.092	220
Pyrolysis off-gas	55	1.148	183
Standard rubber black "B"	55	1.142	194
Pyrolysis off-gas	75	1.190	133
Standard rubber black "B"	75	1.190	135
Pyrolysis off-gas	100	1.282	160
Standard rubber black "B"	100	1.275	163

been commented on before (13), and is out of line with the general relation existing between the concentration of a filler and the abrasion resistance.   It is perhaps a spurious effect due to some lubricating power possessed by the base mix that protects it from the abrasive paper of the machine.   Accelerated abrasion tests carried out by special machines of this nature are far from satisfactory, as shown by a number of investigators, and this phenomenon may be added to the list of uncertainties.

Conclusion

It has been shown that the yield of carbon black that may be obtained from any mixture of hydrocarbon gases is strongly influenced by the presence of olefines; in fact, it has appeared that in the pyrolysis of off-gas mixtures, the olefines are largely responsible for the production of carbon black.   In mixtures of ethylene, methane and hydrogen, the methane may be replaced by hydrogen to a very considerable extent without an appreciable effect on the yield.

The most efficient utilization of hydrocarbon gases of the type of butane and propane for the production of carbon black by the impingement method consists of preliminary pyrolysis of the gases to produce olefines and a certain amount of polymerized aromatic liquids, with the subsequent utilization of the waste gas in a channel plant of the usual type.

It must be remembered that the yields that appear in the major part of this research do not represent the maximum values that could be obtained from the gases.   If very small tips, in relation to the size of the channel, were employed, yields up to 5 lb. per 1000 cu. ft. were obtained.   When the correction due to expansion is applied, a yield of 10 lb. per 1000 cu. ft. of original gas is obtained.   This value represents a theoretical recovery of almost 10%, a very good value for the channel process which, of itself, can seldom achieve more than 6%.   These results are made possible by the fact that the production of olefines in the pyrolysis furnace produces a partial cracking of the gas, so that in effect a smaller part of this operation must be carried out in the flame.   This results in the conservation of carbon.

The carbon produced by this process is of a quality that compares favorably with the best commercial rubber blacks obtainable at present.   The fact that a carbon that has proved to be so similar to a commercial black made from paraffin hydrocarbon gases may be produced in a laboratory plant by the use of a different gas, and, of necessity, an arrangement of burners very different from that used in the large-scale carbon black plants, may be regarded as a proof of the inherent simplicity of the flame impingement process.   It appears that a good black may be produced if a luminous flame is made to impinge, under relatively uniform conditions productive of maximum yield.   The principal factors controlling this yield are the richness of the gas, the shape of the flame, and the position of the depositing surface in the flame, the first two factors being fixed in any given case, and the last readily ascertainable.

The relation between the controllable variables of production and the subsequent properties of the carbon will form the substance of the next paper in this series.

Acknowledgment

The author wishes to acknowledge his indebtedness to Dr. A. Cambron and Mr. C. H. Bayley, who provided the gases used in this research, to Mr. G. Stewart, who carried out the rubber testing, and to Dr. G. S. Whitby, Director of the Division of Chemistry, at whose suggestion the work was undertaken.

References

1. CAMBRON, A. and BAYLEY, C. H.   Can. J. Research, 9 : 175-196.   1933.
2. CAMBRON, A. and BAYLEY, C. H.   Can. J. Research, 9 : 583-590.   1933.
3. CAMBRON, A. and BAYLEY, C. H.   Can. J. Research, 9 : 591-602.   1933.
4. CAMBRON, A. and BAYLEY, C. H.   Can. J. Research, 10 : 145-163.   1934.
5. CRANOR, D. F. and BRAENDLE, H. A.   India Rubber World, 79 : 67-68.   1929.
6. DROGIN, I.   India Rubber J. 110 : 259-274.   1935.
7. FRANCIS, A. W.   Ind. Eng. Chem. 23 : 612-617.   1931.
8. GOODWIN, N. and PARK, C. R.   Ind. Eng. Chem. 20 : 706-715.   1928.
9. GRENQUIST, E. A.   Ind. Eng. Chem. 20 : 1073-1078.   1928.
10. PIDGEON, L. M.   Can. J. Research, B, 13 : 351-369.   1935.
11. PIDGEON, L. M.   Can. J. Research, B, 14 : 127-137.   1936.
12. PLUMMER, W. B. and KELLER, T. P.   Ind. Eng. Chem. 22 : 1209-1211.   1930.
13. THE VANDERBILT NEWS, Vol. 3, No. 3.   R. T. Vanderbilt Company, New York.   1933.
14. WIEGAND, W. B.   Ind. Eng. Chem. 23 : 178-181.   1931.

NOTE ON THE DIFFRACTION OF X-RAYS BY OLD SPECIMENS OF "FROZEN" RUBBER[1]

By William H. Barnes[2]

Abstract

Monochromatic X-ray pin-hole diffraction photographs of two old specimens of "frozen" rubber are described. Histories of the specimens are given. Results are compared with existing data for "frozen" rubber and for fresh stretched rubber. Detailed figures for both conditions are thus made available and confirm the reported identity of their diffraction effects.

Introduction

The object of the present note is to make available in the literature a detailed comparison of the X-ray diffraction effects from old specimens of "frozen" rubber with available data for stretched fresh rubber. Several X-ray diagrams of "frozen" rubber have been published (2, 3), and Ott (6) has recorded measurements made on a photograph of (apparently) "frozen" crepe. Although Ott's values have been confirmed in Clark's laboratory (1) they appear to be the only values readily available in the literature and are rather meagre.

Discussion

The two specimens that form the subject of the present note were examined for Dr. G. S. Whitby and were supplied by him. They will be designated *A* and *B* hereafter. *A* was a pale thin unsmoked sheet made in the Malay States in 1905 and kept in the Imperial Institute, London, until it was turned over to Dr. Whitby in 1925. It was then in the "frozen" condition and has, therefore, been in this condition for at least 11 yr. and probably for 30 yr. *B* was a piece of smoked sheet made by Dr. Whitby in 1913 and has certainly been in the "frozen" condition for 22 yr. The "thawing point" of both samples was approximately 41° C. (7, Chap. 3). This is the temperature at which, after heating for two hours, the samples lose their stiffness and become clear. The densities (15°/15°) of these "frozen" specimens were: *A*, 0.9436; *B*, 0.9347. After "thawing", by heating at 50° C. for two and one-half hours, the densities (15°/15°) dropped to—*A*, 0.9233; *B*, 0.9184. The writer is indebted to Dr. Whitby for the density determinations. As a test of this "thawing" procedure a sample of *A*, after being photographed in the "frozen" condition, was suspended in water at 50° C. for two and one-half hours and then rephotographed. The well defined powder pattern characteristic of diffraction diagrams obtained from "frozen" rubber was found to have been replaced by the strong single halo characteristic of unstretched fresh rubber. The spacing corresponding to this halo was about 4.7Å as compared with 4.5 Å reported by Katz (3) for "thawed" rubber and 4.6 ± 0.1 Å reported

by Mark and von Susich (5) for fresh unstretched rubber. The weak halo at 8.0 Å also observed by Mark and von Susich does not appear in the present photograph.

Identical diagrams consisting of 13 sharply defined haloes were obtained from the two "frozen" specimens A and B. In general characteristics the photographs are typical of those usually obtained from finely powdered organic crystals.

Results

The X-ray data are summarized in Table I: first column, present note (specimens A and B); second column, Ott's values (6) for "frozen" rubber; third column, corresponding figures of Mark and von Susich (5) for stretched

TABLE I

SUMMARY OF RESULTS

A and B	Ott (6)	Mark and von Susich (5)	Lotmar and Meyer (4)
0.123 s.	0.121 w.	0.1251 v.s.	0.1225 s.
—	—	—	0.140 v.w.
0.155 v.s.	0.153 s.	0.156 s.	0.154 s.
0.183 v.s.	0.182 s.	{ 0.1851 v.s. 0.189 m.	{ 0.182 v.s. 0.188 m.
0.206 s.	0.192 w.	{ 0.194 v.s. 0.208 m. 0.212 w.	{ — 0.205 m.s. 0.208 w.
0.226 m.	0.224 w.	{ 0.227 m. 0.228 m.	{ 0.223 w. 0.223 m.
0.255 w.m.	0.240 v.w.	{ 0.248 m. 0.262 w.	{ 0.245 w. 0.256 w.
0.277 w.	0.265 v.w.	{ — 0.279 w.	{ 0.270 v.w. 0.277 w.
0.298 m.	0.289 v.w.	{ — 0.293 v.w. 0.300 w. 0.308 w.	{ 0.299 v.w. 0.300 v.w. 0.299 w. —
0.319 v.w.	—	0.323 v.w.	0.322 v.w.
—	—	—	0.336 v.w.
0.345 w.m.	—	{ 0.350 w. —	{ 0.345 v.w. 0.350 v.w.
0.372 w.m.	—	{ — 0.375 m. —	{ 0.370 w. 0.374 v.w.
0.398 w.	—	0.388 w.	0.400 v.w.
0.418 v.w.	—	—	—

fresh rubber; fourth column, more recent data of Lotmar and Meyer (4) for stretched fresh rubber. Data are recorded in terms of $\sin \theta$ values for $Cu_{K\alpha}$ ($\lambda = 1.54$ Å) radiation; the figures of Ott (iron target, $\lambda = 1.93$ Å) were recalculated for copper, and those of Lotmar and Meyer ($\sin \theta/\lambda$) were multiplied by $\lambda(1.54)$. Visually estimated intensities are indicated ($m =$ medium, $s =$ strong, $v =$ very, $w =$ weak). The brackets in Columns 3 and 4 serve to group fibre spots which would lead to powder haloes unresolvable at the crystal-to-plate distances employed for the data of the first two columns. It will be seen that the agreement among the four columns is very good, and that the present more definite powder photographs of "frozen" rubber yield data in even better accord with those from stretched fresh rubber than do those of Ott (6).

References

1. CLARK, G. L.   Ind. Eng. Chem. 18 : 1131-1136.   1926.
2. HAUSER, E. A.   Kautschuk, 17-21.   1927.
3. KATZ, J. R.   Ergeb. exakt. Naturw. 4 : 161-162.   1925.
4. LOTMAR, W. and MEYER, K. H.   Monatsh. 69 : 115-124.   1936.
5. MARK, H. and VON SUSICH, G.   Kolloid-Z. 46 : 11-21.   1928.
6. OTT, E.   Naturwissenschaften, 14 : 320.   1926.
7. WHITBY, G. S.   J. Am. Chem. Soc. Monograph on rubber.   1937.

PLATE 1
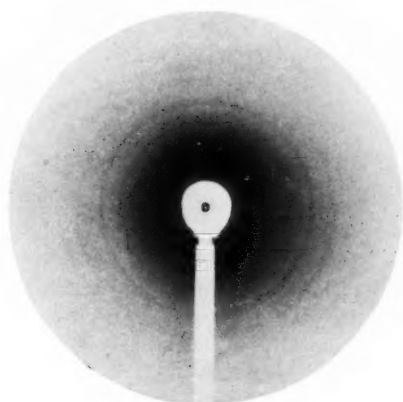
Debye-Scherrer rings from an old sample of "frozen" raw rubber
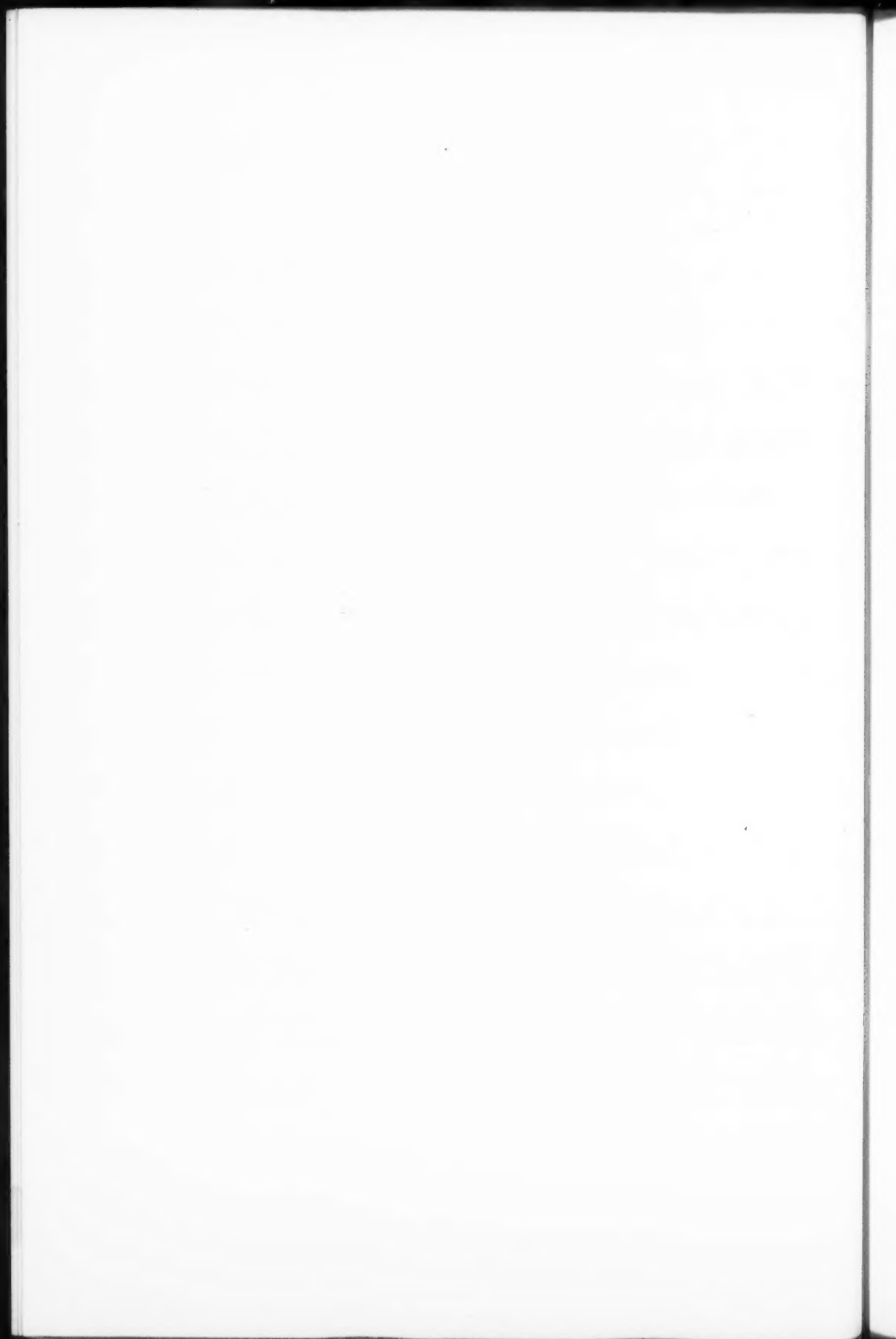
THE ALKALOIDS OF FUMARIACEOUS PLANTS

XIV. CORYPALLINE, CORLUMIDINE AND THEIR CONSTITUTIONS[1]

By Richard H. F. Manske[2]

Abstract

Corypalline, $C_{11}H_{15}O_2N$, a new phenolic alkaloid from *Corydalis pallida* and from the seeds of *C. aurea*, on methylation yielded the known 2-methyl-6 : 7-dimethoxy-tetrahydro-isoquinoline. On ethylation it yielded 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline identical with a specimen synthesized for purposes of comparison. Corypalline therefore is 2-methyl-6-methoxy-7-hydroxy-tetrahydro-isoquinoline, a synthesis of which was achieved.

Oxidative fission of corlumidine O-ethyl ether yielded a base identical with a synthetic specimen of 1-hydroxy-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline. Treatment of the degradative as well as the synthetic base with alkali yielded the corresponding 1-keto-isoquinoline. Corlumidine therefore is 7-O-desmethyl-corlumine.

Syntheses of 2-methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline and the corresponding 1-keto-derivative are described.

During a preliminary investigation of the alkaloids of *Corydalis pallida* Pers., a Japanese species, a small amount of a phenolic alkaloid, melting at 168° C.*, was isolated, for which the name *corypalline* is now proposed. Recent work on the seeds of *C. aurea* has disclosed corypalline as one of the constituents. Analyses yielded figures in agreement with $C_{11}H_{15}O_2N$ and one methoxyl group was indicated. Methylation with diazomethane yielded a monomethyl ether, $C_{12}H_{17}O_2N$, which crystallized as the hemihydrate and which proved to be identical with 2-methyl-6 : 7-dimethoxy-tetrahydro-isoquinoline, previously obtained from adlumine (3) and corlumine (4). Only two structures (I, II) are therefore possible for corypalline. Ethylation
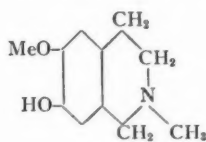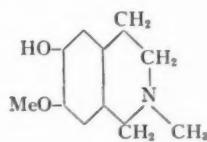
(I)   (II)

with diazoethane yielded a crystalline base, $C_{13}H_{19}O_2N$, melting at 65° C., and this proved to be identical with a synthetic specimen of 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline. The latter was prepared by methylating 6-methoxy-7-ethoxy-3 : 4-dihydro-isoquinoline (8) with methyl iodide and reducing the resultant quaternary iodide with tin and hydrochloric acid. Corypalline therefore is 2-methyl-6-methoxy-7-hydroxy-tetrahydro-isoquinoline (I).

A synthesis of corypalline was accomplished by a route parallel to that used by Späth, Orechoff and Kuffner (10) in their synthesis of salsoline. Ring closure of the formyl derivative of β-(3-methoxy-4-benzyloxy-phenyl)-ethylamine yielded 6-methoxy-7-benzyloxy-3 : 4-dihydro-isoquinoline, which was then methylated with methyl iodide to the quaternary iodide. Reduction of the latter with tin and hydrochloric acid served, in the same operation, to remove the benzyl group. The resulting phenolic base was identical with corypalline in all respects.

With the exception of hydrohydrastinine found in minute quantity in *C. cava* (9), corypalline is the simplest alkaloid thus far found in any species of Fumariaceae, although salsoline (Chenopodiaceae) and pectenine (Cactaceae) from other sources are closely related.

In a previous communication the author proved, by methylation with diazomethane to corlumine, that corlumidine isolated from *C. scouleri* (4) possessed either one of the structures (III) or (IV). Owing to the co-presence of scoulerine (5) in the same botanical source, the expression (III) was preferred.
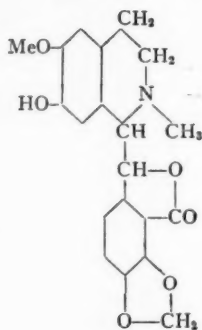
(III)   (IV)
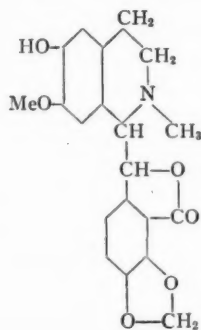
In this eventuality, corlumidine O-ethyl ether on oxidative fission may be expected to yield an amino-aldehyde which on treatment with alkali (Cannizzaro) should be convertible into corypalline O-ethyl ether, together with the corresponding 1-keto-derivative. The result of the experiment was the isolation of a base as picrate, together with the neutral product, but the picrate was not identical with that of corypalline O-ethyl ether. The obvious, though erroneous, interpretation was that corlumidine is (IV), and that the ultimate degradative base was 2-methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline. A synthesis of this base by a procedure strictly analogous to that of corypalline O-ethyl ether failed, however, to establish the identity of the two substances, and the synthetic 1-keto-derivative was not identical with the neutral product from corlumidine. It was ultimately realized that the result of the Cannizzaro reaction was as originally anticipated. The picrate

which was obtained, was, however, that of 1-hydroxy-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline (V),

(V)

(VI)
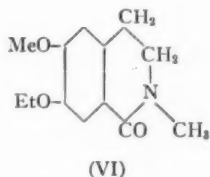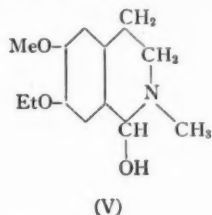
namely, the unchanged hydrolytic base. Owing to the small amounts of material available the more soluble picrate of corypalline O-ethyl ether was lost in the filtrate. A synthesis of the hydroxy-isoquinoline (V) was readily achieved by treating the methiodide obtained during the synthesis of corypalline O-ethyl ether with potassium hydroxide at low temperature. The resulting rearrangement, which is well known in bases of this type, proceeded readily, and the picrate of the synthetic base (V) was identical with that from corlumidine. Finally, the hydroxy-base (V) on treatment with alkali was converted into corypalline O-ethyl ether and the corresponding keto-compound (VI), which proved to be identical with the neutral compound obtained from corlumidine, which is, therefore, represented by (III).

The β-arylethyl-amines required in the syntheses of the methoxy-ethoxy-isoquinolines were prepared by a route involving the Curtius reaction, coupled with a conversion to the phthalimide (2) and hydrolysis of the latter with hydrazine (1).

Experimental

Methylation of Corypalline

A solution of corypalline (50 mg.) in methanol was treated with an ethereal solution of diazomethane, and after 24 hr. the organic solvents were boiled off. The residue was dissolved in dilute hydrochloric acid and the filtered solution basified with excess potassium hydroxide. The liberated base was extracted with ether, dried with potassium carbonate, and the solution evaporated to a small volume. The hemihydrate, which readily crystallized, melted at 82° C., and when admixed with a specimen from adlumine (3) the mixture melted at 82–84° C. Calcd. for $C_{12}H_{17}O_2N \cdot \frac{1}{2}H_2O$; C, 66.67; H, 8.33; N, 6.48; 2 OMe, 28.70%. Found: C, 66.56; H, 8.41; N, 6.48; OMe, 28.04%.

The picrate was recrystallized from benzene-methanol; it melted at 160° C. either alone or in admixture with an authentic specimen of 2-methyl-6 : 7-dimethoxy-tetrahydro-isoquinoline picrate.

Ethylation of Corypalline

The ethyl ether of corypalline was obtained by the procedure outlined for the preparation of the methyl ether. It crystallized with great facility, and was recrystallized from purified hexane in which it is only sparingly soluble.

Long fine needles, which melt at 65° C., were thus obtained. The picrate is sparingly soluble in cold methanol; it was recrystallized from the boiling solvent. It consisted of pale yellow fine prisms melting sharply at 136° C.

β-(3-Methoxy-4-ethoxy-phenyl)-propion-hydrazide

β-(3-Methoxy-4-ethoxy-phenyl)-propionic acid (6) was esterified with methanol in the presence of sulphuric acid and the ester was isolated in the usual way. It was purified by distillation *in vacuo*, and on cooling it solidified completely, melting sharply at 46° C. To prepare the hydrazide a mixture of 47.6 gm. of the methyl ester and 10 gm. of hydrazine was treated with sufficient methanol to yield a homogeneous solution and then heated on a steam bath in an open flask for 16 hr. The solid cake of hydrazide thus obtained was of sufficient purity for the next stage in the synthesis. A small portion was recrystallized from hot methanol in which it is moderately soluble, and the hydrazide then consisted of colorless prisms melting at 124° C. Calcd. for $C_{12}H_{18}O_3N_2$; N, 11.76%. Found: N, 11.19%.

A small amount of a very sparingly soluble by-product, melting at 201° C., was present in the hydrazide. This is evidently the diacyl hydrazide since hydrolysis with potassium hydroxide regenerated the aryl-propionic acid. The same disubstituted hydrazide was obtained as a by-product during the conversion of the hydrazide into the azide. Such a secondary course during the preparation of azides is not new and has been frequently observed by the author.

β-(3-Methoxy-4-ethoxy-phenyl)-ethylamine

The synthesis of this amine was described by Späth and Dobrowsky (8) who obtained it by way of the corresponding nitro-styrene. Intermediates were not isolated in the following synthesis. A solution of 12 gm. of the above-mentioned hydrazide in 50 cc. of acetic acid was cooled by adding crushed ice and then treated with an aqueous solution of 4 gm. of sodium nitrite. The precipitated azide soon crystallized. It was filtered off, washed with water and thoroughly drained at the pump. The somewhat pasty product was decomposed by gradual addition to boiling methanol. On cooling, a small amount of the diacyl hydrazide separated and this was filtered off. It may be noted that the azide prepared from the carefully purified hydrazide also yielded this by-product. The filtrate, which contained the methyl urethane and the dialkyl urea, was evaporated to a thick syrup. It was treated with 7.4 gm. of phthalic anhydride (2) and heated in an oil bath for 15 min. at 225–230° C. The cooled mixture was treated with a little methanol and the excess anhydride removed by adding aqueous sodium bicarbonate. The oily phthalimide was taken up in ether and the washed solution dried, filtered, and evaporated. The residue from two such experiments weighed 22 gm. It was treated with 4 gm. of hydrazine (1) in a little methanol and heated on the steam bath. Crystallization of phthalyl hydrazide was almost immediate. The methanol was boiled off and water and excess potassium hydroxide added, and the mixture exhausted with ether. The combined

extract was washed with a little water and the amine then extracted with several successive portions of dilute hydrochloric acid. Regeneration of the amine from the acid solution and extraction with ether yielded 4.0 gm.

The ethereal solution from which the amine had been extracted yielded, on drying and evaporating, an oily residue that crystallized almost completely in the course of several days. It was drained at the pump and recrystallized first from benzene-petroleum ether and then from dilute methanol; it consisted of colorless rectangular plates melting sharply at 81° C. This proved to be the N-carbomethoxy derivative of the amine, and its presence here was due to incomplete reaction with the phthalic anhydride. Calcd. for $C_{13}H_{19}O_4N$; C, 61.66; H, 7.51; N, 5.53%. Found: C, 61.76; H, 7.47; N, 5.80%.

In a second experiment the azide was extracted with ether from the acetic acid mixture. Some sparingly soluble diacyl hydrazide was removed by filtration and the ethereal solution thoroughly washed finally with aqueous sodium bicarbonate. The ether was distilled from small successive portions and the residual azide decomposed by gentle warming with water. The resulting sym-di-β-(3-methoxy-4-ethoxy-phenyl)-ethyl urea crystallized readily and when recrystallized from hot methanol it melted at 154° C. Calcd. for $C_{23}H_{32}O_5N_2$: N, 6.42%. Found: N, 6.64%.

It was converted into the phthalimide as above. Recrystallized from hot methanol, β-(3-methoxy-4-ethoxy-phenyl)-ethyl-phthalimide was obtained in colorless moderately soluble needles melting at 84° C. Calcd. for $C_{19}H_{19}O_4N$: N, 4.31%. Found: N, 4.34%.

During the conversion of this crude phthalimide into the amine a substance sparingly soluble in ether was obtained. It was recrystallized from methanol in which it is moderately soluble; it then consisted of large colorless plates melting at 127° C. Analyses show that this is β-(3-methoxy-4-ethoxy-phenyl)-propion-β-(3-methoxy-4-ethoxy-phenyl)-ethyl amide. Calcd. for $C_{23}H_{31}O_5N$; C, 68.83; H, 7.73; N, 3.49%. Found: C, 68.48; H, 7.80; N, 3.71%.

2-Methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline

The amine described above (4.0 gm.) was converted by the procedure of Späth and Dobrowsky into 6-methoxy-7-ethoxy-3 : 4-dihydro-isoquinoline. There was obtained 2.2 gm. of crystalline base which was treated with excess methyl iodide in methanol. The solid crystalline cake of methiodide, which separated in the course of 30 hr., was dissolved in hot water, and the filtered solution heated on the steam bath overnight with 25 cc. of concentrated hydrochloric acid and finely granulated tin. The aqueous decantate was diluted somewhat and most of the tin precipitated with hydrogen sulphide. The clear filtrate from which the excess hydrogen sulphide had been removed was basified with excess potassium hydroxide and the liberated base extracted with ether. The ether extract was evaporated somewhat, filtered with the addition of a little charcoal, and evaporated to a thin syrup. The colorless crystals that separated were washed with petroleum ether and recrystallized from a mixture of ether and hexane. Washing with the latter solvent and

drying *in vacuo* yielded pure 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline melting sharply at 65.5° C., and this melting point was not depressed when the substance was mixed with a specimen of corypalline ethyl ether.   Calcd. for $C_{13}H_{19}O_2N$: N, 6.34%.   Found: N, 6.23%.

The picrate was recrystallized from hot methanol; it melted at 136° C. either alone or in admixture with a specimen of corypalline ethyl ether picrate.

Synthesis of Corypalline

The requisite β-(3-methoxy-4-benzyloxy-phenyl)-ethylamine was prepared from benzyl vanillin by the method described by Späth and co-workers (10). From 46 gm. of vanillin there was obtained 2.1 gm. of the amine which was treated with 2 cc. of anhydrous formic acid and heated on a steam bath for five hours.   The product was heated in an oil bath at 170–180° C. for 30 min., dissolved in toluene, heated to boiling and treated with 4 gm. of phosphorus pentoxide in small successive portions.   The toluene was decanted from the dark pasty residue and the latter decomposed with ice and a little hydrochloric acid.   The boiled and filtered solution (charcoal) was basified with ammonia and the liberated base extracted with several successive portions of ether. Evaporation of the extract yielded the dihydro-isoquinoline which solidified on cooling.   It was dissolved in a small volume of methanol and 2 gm. of methyl iodide added.   After 36 hr. the solvents were evaporated and the filtered solution of the residue was treated with 15 cc. of concentrated hydro-chloric acid and heated on a steam bath for 24 hr. with excess tin.   The tin in the solution was removed by means of metallic zinc and the filtered solution basified with excess ammonia.   The ether extract from the basic solution crystallized when evaporated to a small volume, and the base thus obtained melted at 166° C.   Yield, 0.2 gm.   It crystallized with great facility when a concentrated methanolic solution was treated with a little dry ether in which it is sparingly soluble.   As thus obtained synthetic corypalline consisted of colorless, well formed prisms, melting sharply at 168° C.   Corypalline of natural origin also melts at 168° C., and in admixture with a synthetic specimen there was no depression in melting point.

The picrate was recrystallized from hot methanol in which it is sparingly soluble.   Pale yellow needles melting at 178° C. were thus obtained.   A specimen of corypalline picrate prepared from the alkaloid from the seeds of *Corydalis aurea* melted at 178° C., and a mixture of the two products melted at the same temperature.

Ethylation and Degradation of Corlumidine

A suspension of 0.8 gm. of corlumidine in 50 cc. of chloroform was treated with an ethereal solution of diazoethane.   Evolution of nitrogen and dissolution of the alkaloid gradually ensued.   After 24 hr. the ether was boiled off and a second portion of ethereal diazoethane added.   When the alkaloid was completely dissolved and the evolution of nitrogen ceased, the solution was evaporated to dryness and the residue dissolved in dilute hydrochloric acid. The filtered solution was basified with ammonia and the liberated base ex-

tracted with a mixture of ether and chloroform. Removal of the solvent yielded an almost colorless resin which failed to crystallize in contact with methanol. The solvent was completely removed *in vacuo* and the corlumidine ethyl ether heated for 20 min. with 8 cc. of dilute nitric acid prepared by diluting 2 cc. of concentrated nitric acid to 10 cc. with water. The cooled solution was rendered alkaline by the addition of excess potassium hydroxide and the basic hydrolytic fragment extracted with ether. Parenthetically it may be mentioned that the alkaline solution on appropriate treatment readily yielded 3 : 4-methylene-dioxy-phthalide, a rather superfluous observation, but nevertheless a confirmation of the structure of the phthalide moiety. The ether extract was freed of solvent and the basic residue heated with methanolic potassium hydroxide on the steam bath for one hour. Water was added and the methanol boiled off. The insoluble oil was taken up in ether and the solution cautiously washed with water. It was then shaken with several successive portions of dilute hydrochloric acid and the base regenerated from the acid extract. It was again taken up in ether and the residue from this dissolved in boiling hexane. The filtered extract was evaporated to a small volume but did not crystallize readily. It was converted into the picrate which was recrystallized from hot methanol in which it is sparingly soluble. Orange-yellow fine prisms of 1-hydroxy-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline picrate, melting at 180° C., were thus obtained.

The ether solution from which the above base had been extracted was dried with potassium carbonate and the ether largely distilled. Cautious addition of hexane yielded large colorless plates of 1-keto-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline melting sharply at 121° C.

1-Hydroxy- and 1-Keto-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline

The methiodide from 2.0 gm. of 6-methoxy-7-ethoxy-dihydro-isoquinoline was dissolved in a small volume of water, and the cooled solution rendered strongly alkaline by the gradual addition of potassium hydroxide. The semi-solid precipitate was separated from the alkaline solution by repeated extraction with ether. Removal of the ether yielded a pale yellow, partly crystalline mass.

A small portion of this was converted into the picrate in hot methanol, and the orange crystals which were thus obtained melted at 181° C. In admixture with the picrate from the degradation of corlumidine, there was no depression in the melting point. Calcd. for $C_{19}H_{22}O_{10}N_4$: N, 12.02%. Found: N, 12.40%.

The remainder of the base was heated for several hours on the steam bath with aqueous methanolic potassium hydroxide and then the methanol evaporated. The residue was extracted with several successive portions of ether and the combined extract washed with water. It was then extracted with dilute hydrochloric acid, from which extract a small amount of 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline was isolated, but only with difficulty. The ethereal solution was evaporated and the crystalline residue recrystallized from dry ether. Colorless elongated plates of 1-keto-2-methyl-

6-methoxy-7-ethoxy-tetrahydro-isoquinoline were thus obtained. This substance, either alone or in admixture with a specimen of the neutral degradative product from corlumidine, melted sharply at 121° C., and the melt readily crystallized again on slight cooling. Calcd. for $C_{13}H_{17}O_3N$; N, 5.96%. Found: N, 6.14%.

Isovanillin Ethyl Ether

The ethylation of isovanillin with diethyl sulphate does not appear to have been previously described. A suspension of 30.4 gm. of isovanillin in 34 gm. of diethyl sulphate is treated with 10 cc. of ethanol and a concentrated aqueous solution of 12 gm. potassium hydroxide slowly added with vigorous agitation. Toward the end of the addition gentle heating is desirable and a little more potassium hydroxide may be added to ensure alkalinity of the mixture. The oil is extracted with ether, washed with aqueous potassium hydroxide and with water. Removal of the ether and drying on a steam bath yields an almost colorless residue which solidifies completely on cooling and weighs 35 gm. (97% of theory). On distillation *in vacuo* it may be obtained colorless and the yield then is 31–32 gm. Oxidation with alkaline permanganate yielded the known 3-ethoxy-4-methoxy-benzoic acid melting at 165° C.

β-(3-Ethoxy-4-methoxy-phenyl)-propionhydrazide

The methyl ester of the propionic acid (6) was readily prepared in 90% yield by esterification in the presence of sulphuric acid. It was obtained as a colorless viscous liquid boiling at 166° C. at 4 mm. The methyl ester (43 gm.) was heated on a steam bath for 16 hr. with hydrazine (11 gm.) and a little methanol. The completely solid residue was of sufficient purity for the preparation of the azide. A portion was recrystallized from hot methanol in which it is readily soluble. Colorless fine needles, melting at 124° C., were thus obtained. Calcd. for $C_{12}H_{18}O_3N_2$: N, 11.76%. Found: N, 11.19%.

β-(3-Ethoxy-4-methoxy-phenyl)-ethylamine

The azide was prepared by the procedure outlined in the case of the isomer, but owing to the fact that it did not crystallize it was extracted with ether. At this point a small amount of the diacyl hydrazide separated in the aqueous phase. The ethereal solution was washed with water and then with aqueous sodium bicarbonate. A small portion of the ether extract was evaporated and the residue decomposed by gentle heating with water. The accumulated dialkyl-urea served as a diluent for the decomposition of subsequent portions of the azide which were added progressively until a total of 42 gm. of hydrazide had been used. The oily product was finally dissolved in ether and filtered from a further small amount of diacyl-hydrazide. Evaporation of the solvent from the filtrate yielded a residue weighing 20 gm. This product, which consisted essentially of the dialkyl-urea, was worked up as in the case of the isomer. It yielded 5.2 gm. of the arylethylamine.

Sym-Di-β-(3-ethoxy-4-methoxy-phenyl)-ethyl Urea and the Phthalimide

The crude urea in contact with ether readily crystallized. It was washed with ether and recrystallized from hot methanol in which it is readily soluble. Large colorless prisms, melting at 137° C., were thus obtained. Calcd. for $C_{23}H_{32}O_5N_2$: N, 6.42%. Found: N, 6.94%.

When the urea is heated with phthalic anhydride under the standard conditions, it is converted into the corresponding phthalimide. The latter was isolated in the usual way and when recrystallized twice from hot methanol, long, stout needles were obtained. β-(3-Ethoxy-4-methoxy-phenyl)-ethyl phthalimide is sparingly soluble in cold methanol and melts at 116° C. Calcd. for $C_{19}H_{19}O_4N$: N, 4.31%. Found: N, 4.35%.

2-Methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline

The procedure detailed in the case of the 6-methoxy-7-ethoxy analogue yielded 2.2 gm. of 6-ethoxy-7-methoxy-3 : 4-dihydro-isoquinoline from 5 gm. of the above-mentioned amine. It was converted into the methiodide with methyl iodide. A portion of the latter was reduced with tin and hydrochloric acid. The resulting tertiary base crystallized readily, and when recrystallized from dry ether it consisted of long needles and melted sharply at 76° C. Calcd. for $C_{13}H_{19}O_2N$: C, 70.59; H, 8.60; N, 6.34%. Found: C, 70.51; H, 8.54; N, 6.26%.

The picrate is moderately soluble in methanol. It crystallized from this solvent in pale yellow plates melting at 120° C.

1-Keto-2-methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline

A second portion of the methiodide, from which the above tertiary base was prepared, was treated with solid potassium hydroxide in concentrated aqueous solution. The liberated base was extracted with ether and then heated with aqueous methanolic potassium hydroxide to bring about the Cannizzaro change. The basic portion of the reaction product was isolated as the picrate, which proved to be identical with that obtained by reducing the quaternary iodide. The neutral fraction crystallized readily and when recrystallized from ether it was obtained in colorless thick plates melting at 96° C. Calcd. for $C_{13}H_{17}O_3N$: N, 5.96%. Found: N, 5.94%.

References

1. ING, H. R. and MANSKE, R. H. F. J. Chem. Soc. 2348-2351. 1926.
2. MANSKE, R. H. F. J. Am. Chem. Soc. 51 : 1202-1204. 1929.
3. MANSKE, R. H. F. Can. J. Research, 8 : 404-406. 1933.
4. MANSKE, R. H. F. Can. J. Research, B, 14 : 325-327. 1936.
5. MANSKE, R. H. F. Can. J. Research, B, 14 : 347-353. 1936.
6. SCHLITTLER, E. Ber. 66 : 988-995. 1933.
7. SPÄTH, E. and BERNHAUER, E. Ber. 58 : 200-204. 1925.
8. SPÄTH, E. and DOBROWSKY, A. Ber. 58 : 1274-1284. 1925.
9. SPÄTH, E. and JULIAN, P. L. Ber. 64 : 1131-1137. 1931.
10. SPÄTH, E., ORECHOFF, A. and KUFFNER, F. Ber. 67 : 1214-1217. 1934.

A FURTHER STUDY OF THE PRETREATMENT OF WOOD IN AQUEOUS SOLUTIONS[1]

BY A. J. COREY[2], J. M. CALHOUN[3] AND O. MAASS[4]

Abstract

The study of the pretreatment of wood has been continued. Wood-meal was heated in buffer solutions at constant temperature for periods of time up to 96 hr. This extreme pretreatment was found to cause the formation of a substance which is determined as lignin by the ordinary methods of analysis. It was found that wood, heated in a buffer solution at pH 3 for 36 hr. at 140° C., could be completely delignified, though at a reduced rate of pulping. Jack pine is shown to give results similar to those obtained with spruce. A physical agglomeration of the lignin particles is proposed as an explanation of the results.

In two previous papers (2, 3) the influence of the heating of wood in aqueous solutions on the rate of its subsequent delignification in sulphite liquor was discussed. On the basis of the experimental data cited, the hypothesis was advanced that the heating of wood in aqueous solutions results in a physical agglomeration of the lignin present, and hence in a reduction of the surface area available for reaction. In the sulphite process this tendency would constantly oppose an acceleration in the cooking rate, which would normally be expected as the sizes of the individual lignin particles were decreased through reaction. The action of these two opposing tendencies was advanced as a possible explanation for the approximately monomolecular rates observed in delignification with sulphite solutions.

If the pH at which the minimum pretreating effect was observed differed from that of sulphite liquor at the cooking temperature, and if the temperature coefficients of the dissolving process and the coagulation process are different, it might be possible to detect a slowing up of the cooking reaction, brought about by a coagulation of the lignin during cooking in sulphite liquor.

The following experiment was designed to test this. Delignification curves for 120° and 140° C. were obtained with chips from the same wood specimen. With a sample of the same wood, a cook was carried out for six hours at 120° C. under conditions identical with those obtaining during the series at 120° and 140° C. After six hours the oil bath was quickly lowered, and a second bath, heated to 140° C., was raised about the cooking cell. The cooking was then continued at the latter temperature for two hours.

In order to make this experiment more easily intelligible a diagram to illustrate the curves at 120° and 140° C. is shown in Fig. 1.

The wood sample was cooked at 120° C. for six hours. It should then have a lignin value given by the point A on the curve for 120° C., which corresponds

to B on the curve for 140° C. From the position of B, the time required to cook to this lignin value at 140° C. could be determined from the delignification curve for 140° C. After two hours' cooking of the product A at 140° C., the equivalent time of cooking at 140° C. for the whole experiment will be
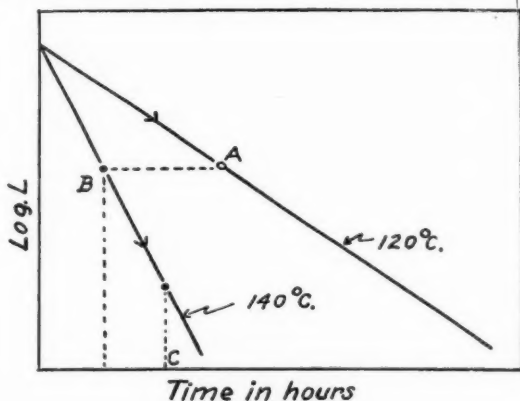

Time in hours
FIG. 1.

given by the position of C. Now if the slow cooking period at 120° C. has favored coagulation of the lignin, the rate of cooking at 140° C. will be less than normal, and the lignin value found for the pulp will be greater than would be obtained if the cooking were actually carried out for C hours at 140° C. The lignin value corresponding to C hours of digestion at 140° C. was found from the curve to be 1.55%.

The lignin value found in this experiment was 1.5%, which was virtually identical with the value that would be obtained if all the cooking had been done at 140° C. for an equivalent length of time. This result agrees with the work of Yorston (10) on the effect of gradual heating in sulphite pulping. He shows that only a very slight, if any, "pretreatment effect" can be detected in this manner.

It would appear that if there is a tendency for the lignin to coagulate during sulphite pulping, the temperature coefficient of this process must be approximately the same as that of the opposing cooking action.

The Variation of Pretreatment Effect with Temperature at Constant pH

The preceding discussion indicates the desirability of gaining further information concerning this change in lignin, which for convenience may be called the pretreatment effect. By pretreating wood-meal in buffer solutions the hydrogen ion concentration could be kept constant and the effect of the temperature alone could be observed.

Samples of spruce wood-meal were pretreated in buffer solutions of pH 3, 5, and 7 for six hours at temperatures of 100°, 110°, 120°, 130°, and 140° C. The pretreatment was carried out in glass-lined bronze bombs. After the

pretreatment the samples were cooked for three hours at 140° C. in bisulphite
liquor of composition: total SO_2, 5.12; free SO_2, 3.90; combined SO_2, 1.22%.
The wood-meal had a density of 0.39 and a lignin content of 30.9%. The
results obtained are listed in Table I.

TABLE I

VARIATION OF PRETREATMENT EFFECT WITH TEMPERATURE AT CONSTANT pH

pH of pretreating solution	Temp. of pretreatment, ° C.	Yield of pulp, %	Carbo- hydrate, %	Lignin in pulp, %	Residual lignin, %
	100	49.8	47.0	5.64	2.81
	100	49.7	46.8	5.86	2.91
3	110	50.0	46.7	6.69	3.34
	110	50.8	47.4	6.64	3.38
	120	53.2	47.4	11.00	5.84
	130	57.0	47.5	16.55	9.46
	100	49.2	46.9	4.77	2.35
	110	49.8	47.5	4.60	2.29
5	120	52.4	48.5	7.47	3.91
	130	55.1	49.3	10.35	5.81
	140	58.9	50.3	14.60	8.60
	100	53.0	49.9	5.83	3.09
	110	54.1	50.0	7.58	4 10
7	130	60.0	52.6	12.4	7.40
	140	64.6	52.6	18.6	12.0

The solutions obtained in the pretreatments at pH 3 were checked with a
quinhydrone electrode after the pretreatment, and were found to have a
pH of about 3.1.

The yields of pulp and the residual lignin values are plotted against the
temperature of pretreatment in Fig. 2. As would be expected, the yields at
pH 7 are higher than those at pH 3 or pH 5, the cellulose being less stable in
acid media. It is strange, however, that the yields of carbohydrate at pH 5 and
pH 7 should increase with increase in the temperature of pretreatment. It is
possible that this phenomenon may be due to a shift of the pH toward the
alkaline side as the temperature is increased. Another peculiar circumstance
found in this series is the fact that the lignin curves for pH 3 and pH 7 cross
at low temperatures. Check runs were made at 100° and 110° C. in solutions
of pH 3, since these results might have been in error owing to a small tem-
perature variation; however, the original results were found to be correct.

The lignin values obtained from the samples that were pretreated in solutions
of pH 5 at 100° and 110° C. are of the same order as those that would be
obtained with no pretreatment, but at higher temperature the lignin values
increase, even for the pretreatments at pH 5. There apparently is no hydro-
gen ion concentration at which wood may be heated in a buffer solution to
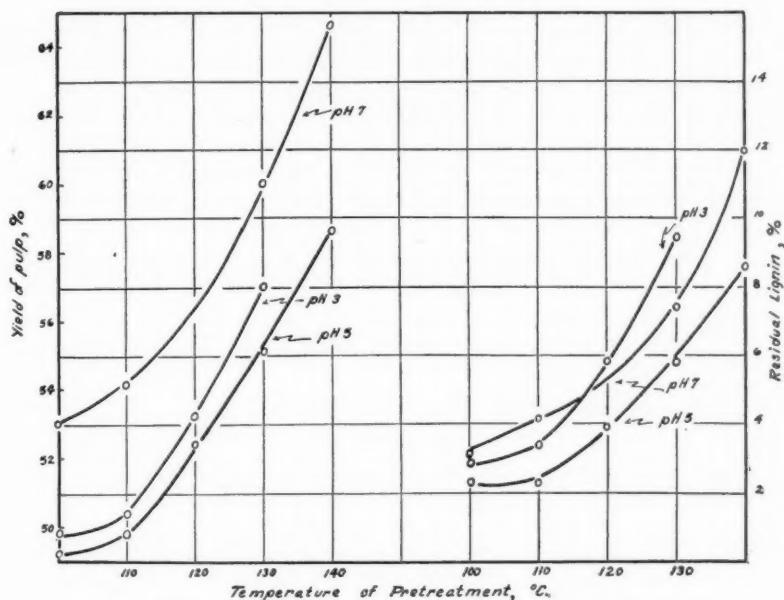temperatures above 120° C. without changing the cooking properties of the

FIG. 2.   *Effect of temperature of pretreatment on subsequent delignification.*

wood to some extent, but, with the McIlvaine buffers used in these experi-
ments, the least effect is always obtained at pH 5, as determined at room
temperature.   This condition might not always hold if different buffers were
used, for two reasons:

(i) Different buffer solutions of the same initial pH value may be altered
to different degrees by the high temperature of pretreatment.

(ii) The effect may be due to the concentrations of the different ions
present, in which case different ionic species will affect the process to different
degrees.   An investigation of this factor has been published separately (1).

From the slopes of the curves in Fig. 2 it appears that the temperature
coefficient of the pretreatment effect is roughly of the same order as the
temperature coefficient of delignification, and the two effects are not separ-
ated in this experiment, so that no quantitative determination can be made.
The similarity in value of these two temperature coefficients would make it
very difficult to detect the presence of a tendency for the lignin to coagu-
late in normal sulphite cooking.

The Variation in Lignin Value with Time of Pretreatment at Constant Temperature and pH

Thus far the experiments on the pretreating of wood had been confined
to six-hour periods, and it was of considerable interest to determine to what
extent the rate of subsequent delignification would be retarded if the pre-

treating process were carried out for longer periods of time. If the pretreatment is carried out sufficiently long a maximum effect is approached, after which further pretreatment will not measurably increase the difficulty of delignifying the wood in sulphite liquor. The determination of the time required to reach this maximum, and the extent to which the lignin will be altered when the maximum is reached, might shed some light on the mechanism involved, and indicate whether it is a chemical or a colloidal change that is taking place.

To this end a series of pretreatments was carried out on samples of spruce wood-meal in solutions of pH 3 and pH 7 at 130° C. After the required period of pretreatment the samples were air-dried, and cooked for three hours at 140° C. in cooking liquor of composition as follows: total SO_2, 5.15; free SO_2, 3.90; combined SO_2 1.25%.

The results of these experiments are reported in Table II.

TABLE II

SPRUCE WOOD-MEAL PRETREATED FOR LONG PERIODS OF TIME IN BUFFER SOLUTIONS AT 130° C.

Time of pretreatment, hr.	Yield of pulp, %	Carbo-hydrate, %	Lignin in pulp, %	Residual lignin, %	Sulphur as	
					Per cent pulp	Per cent lignin
A. Pretreatment solutions of pH 3. Wood: density, 0.39; lignin content, 30.9%						
2	47.2	44.7	5.3	2.5		
4	53.8	46.9	12.7	6.9		
8	58.7	48.6	17.2	10.1		
12	64.3	48.4	24.7	15.9	1.26	5.10
18	65.9	47.8	27.4	18.1	1.34	4.92
24	66.7	46.9	29.7	19.8	1.36	4.57
48	67.3	43.4	35.5	23.9	1.08	3.05
B. Pretreatment solutions of pH 7. Wood: density 0.34; lignin content, 29.0%						
					pH before	pH after
2	56.2	52.0	7.5	4.21	7.01	6.94
5	60 9	53.6	11 9	7 25	7 01	6.87
8	62.5	53.6	14.3	8.94	7.01	6.87
12	66.0	54.8	17.0	11.2	7.01	6.87
18	66.2	51.8	21.7	14.3	7.01	6.83
24	68.4	52.7	23.0	15.7	7.01	6.80

The lignin values in Table II, A, indicate that the pretreating process has not reached a maximum, even after 48 hr. of pretreatment. The amount of lignin remaining in the pulp after three hours of digestion in sulphite liquor increases as the time of pretreatment is increased, and shows no evidence of reaching a point where further pretreatment will not increase the difficulty of delignifying the wood. This fact is emphasized in Fig. 3. Some further information is gained from the sulphur determinations. These values show that the degree of sulphonation of the lignin is decreased by continued pretreatment, and the longer the process is continued, the less sulphonation will be obtained after three hours' cooking in sulphite liquor.

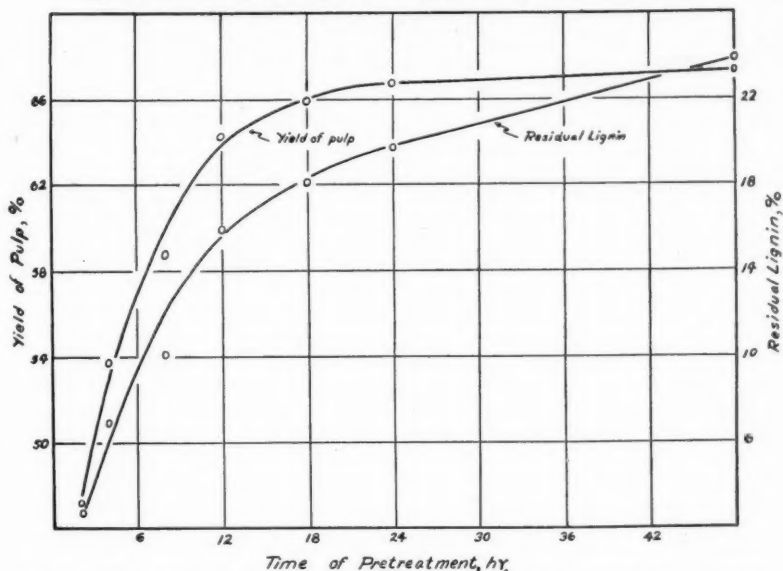FIG. 3.   *Effect of time of pretreatment (pH 3; temp. 130° C.) on subsequent delignification.*

This series could not be continued because no more wood-meal of this sample remained.

The results listed in Table II, *B*, are plotted in Fig. 4.   It should be remarked here that this series is a repetition of work previously reported.
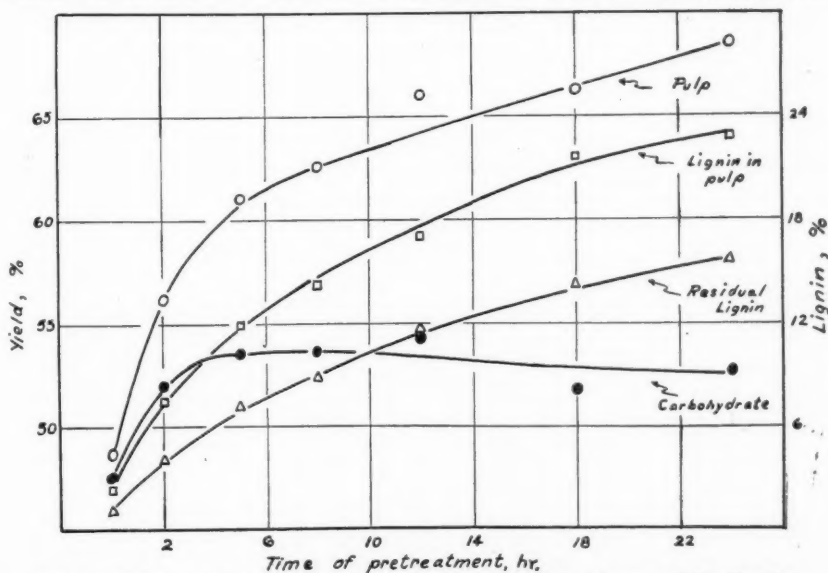

FIG. 4.   *Effect of time of pretreatment (pH 7; temp., 130°C.) on subsequent delignification.*

The experiment carried out previously (3) at pH 7 for eight hours appeared to indicate that the pretreating effect accelerated with increase in time of pretreatment. Such a phenomenon was in disagreement with the results at pH 3 and quite unexplainable. The present experiment at pH 7 carried out for 24 hr. shows a de-acceleration of the pretreating effect with increase in time of pretreatment, in complete agreement with the results at pH 3, the difference in severity being due only to the difference in pH.

It is noted that the yield of carbohydrate first increases with the time of pretreatment, reaches a maximum, and then slowly decreases. The decrease in the yield of carbohydrate after many hours of pretreatment may be due to degradation during pretreatment, simultaneous with the change that decreases the solubility of the lignin. On the other hand, it is possible that the concentration of lignin sulphonic acid in the pulp governs the yield of carbohydrate. After pretreatment the lignin sulphonates more slowly, and hence the carbohydrate material is subjected to a lower acidity within the fibres, and is less degraded in the early stages of pretreatment.

Pretreatment at 140° C.

Since the above experiments indicated that it might be necessary to continue the pretreatments for many hours before a maximum was attained at 130° C., a new supply of spruce wood-meal was prepared, and a series of pretreatments was carried out at 140° C. in solutions buffered to pH 3. The samples were then washed, air-dried, and cooked three hours at 140° C. in cooking liquor of composition: total SO_2, 5.14; free SO_2, 3.90; combined SO_2, 1.20%. A test cook was made on the untreated wood-meal.

The results listed in Table III provide a considerable amount of interesting information. The yields of pulp are seen to increase rapidly up to 18 hr. of pretreatment, and to continue increasing slowly up to a maximum at 72 hr. of pretreatment. After 96 hr. of pretreatment virtually the same yield is obtained after three hours' digestion in sulphite liquor as was obtained after 72 hr. of pretreatment. However, it is obvious that further pretreatment will cause the yields to decrease, since the yields of carbohydrate are being decreased by the severity of the pretreating process.

TABLE III

SPRUCE WOOD-MEAL PRETREATED IN BUFFER SOLUTION, pH 3, 140° C.

Time of pretreatment, hr.	Yield of pulp, %	Yield of carbohydrate, %	Ross-Potter lignin in pulp, %	Ross-Potter residual lignin, %	Madison lignin in pulp, %	Madison residual lignin, %	Sulphur, % of pulp	Sulphur, % of Ross-Potter lignin
0	48.3	47.0	2.58	1.25			0.331	13.4
6	61.9	50.0	19.2	11.9			1.18	6.15
18	66.8	45.1	32.5	21.7	31.8	21.3	1.21	3.73
24	66.8	43.9	34.2	22.9			1.20	3.50
48	67.8	39.6	41.5	28.2	35.3	23.9	1.08	2.61
62	69.0	39.0	43.6	30.0			0.945	2.17
72	70.4	37.8	46.2	32.6			1.10	2.39
96	70.2	36.2	48.4	34.0	39.9	28.1	0.80	1.65

Wood-meal, density, 0.34; lignin content, Madison method, 26.3%; Ross-Potter method, 29.0%.

The lignin values obtained in this series were remarkable. As has been stated previously, by "residual lignin" is meant the quantity of lignin remaining in the pulp after cooking, expressed as a percentage by weight of the original wood sample; or simply—

% Residual lignin = % lignin in pulp × % yield of pulp.

Thus the limiting value for the residual lignin will correspond to the lignin content of the uncooked wood. Table III shows that, after 62 hr. of pretreatment, followed by three hours' cooking at 140° C., not only has no lignin been removed from the wood, but the residual lignin has increased to a value 1% greater than the original lignin content of the wood. On pretreating for longer periods the residual lignin values continue to increase until, after 96 hr. of pretreatment, the residual lignin reaches a value of 34%. One would gather from these results that there is being formed from the wood, either during the pretreatment or the subsequent cooking, some substance that is determined as lignin by the method of Ross and Potter (8). As a check on the above method, lignin analyses were carried out on the 18, 48, and 96 hr. samples, by the use of the Madison method. The results of these analyses (Table III) show that the sample pretreated for 96 hr. had a residual lignin value 2% greater than that of the uncooked wood, as determined by this method; namely, 26.3%.   Evidently a small quantity of this "apparent lignin" is determined even by the Madison method.

The results of the sulphur determinations for this series confirm the previous statement that pretreatment of wood in aqueous solutions at high temperatures makes the lignin more difficult to sulphonate.

The yields of pulp, carbohydrate, residual lignin, and sulphur values are plotted against the time of pretreatment in Figs. 5 and 6.   The curves of the
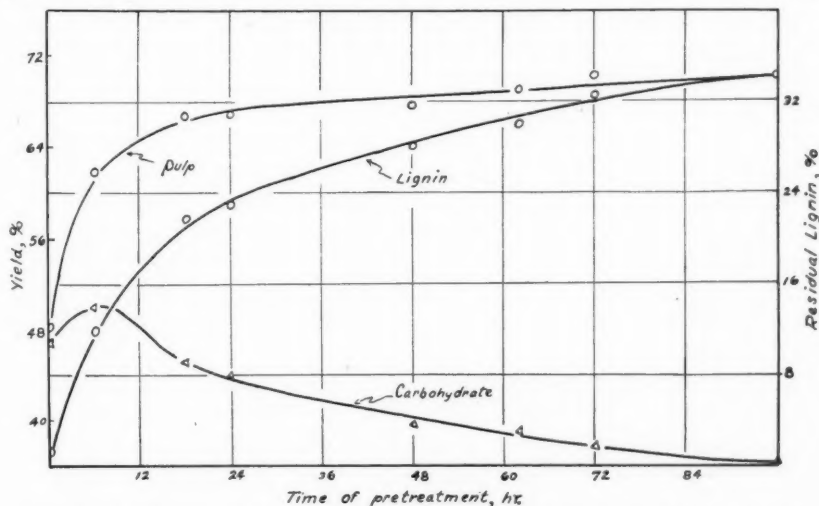

FIG. 5.   Effect of time of pretreatment (pH 3; temp. 140° C.) on subsequent delignification.
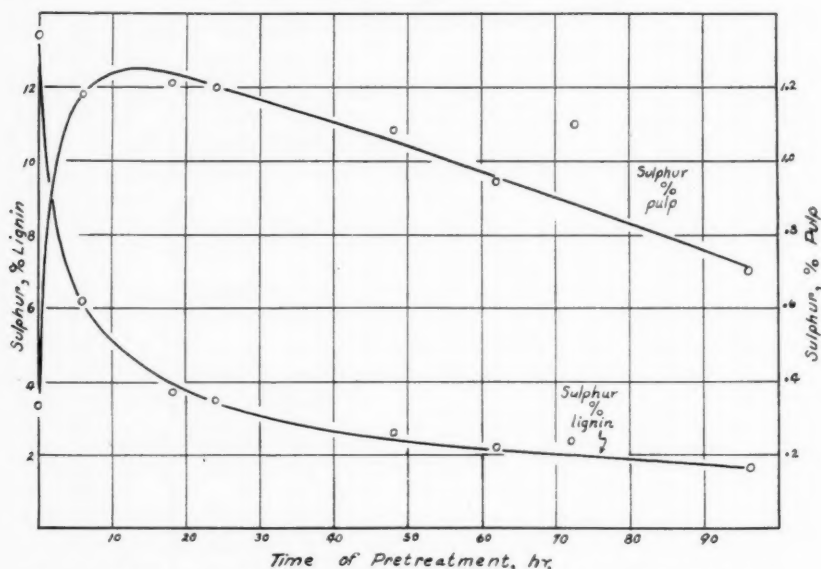
FIG. 6.   *Effect of time of pretreatment (pH 3; temp. 140° C.) on subsequent sulphonation.*

sulphur values are particularly interesting.   The first few hours of pretreatment cause a marked decrease in the amount of sulphonation that can be obtained by three hours of cooking.   Further pretreatment causes the curve to drop more slowly.   The curve of the amount of sulphur expressed as percentage of the pulp is similar in shape to the curve obtained in a normal cooking series, except that the drop after the maximum is reached is more gradual, owing to the fact that very little lignin is being cooked out after 24 hr. of pretreatment.

Investigation of the Formation of Apparent Lignin

In order to obtain a correction for the lignin values in Table III the following experiment was performed. Samples of the same wood-meal as that used in the previous experiment were pretreated in solutions of pH 3 at 140° C. for 12, 24, 48, 72, and 96 hr.   The yields and lignin content of the product were determined, after the pretreatment, as percentage of the uncooked wood-meal.

Lignin determinations by the Madison method were also carried out on the samples that were pretreated 12, 48 and 96 hr.   The complete results are listed in Table IV.

An experiment was also made to determine how the formation of apparent lignin varied with the hydrogen ion concentration of the pretreating solution. Samples of wood-meal were heated in solutions of pH 2.2, 5.0 and 8.0 for 48 hr., but, since the temperature rose to 148° C. during the pretreatment, these results are not comparable with the results of the 48 hr. pretreatment at pH 3, described above.

TABLE IV

THE FORMATION OF APPARENT LIGNIN DURING HEAT PRETREATMENT IN AQUEOUS SOLUTIONS

Time of pretreatment, hr.	Yield of pulp, %	Ross-Potter lignin in pulp, %	Ross-Potter residual lignin, %	Madison lignin in pulp, %	Madison residual lignin, %
0	100	29.0	29.0	26.3	26.3
12	74.4	40.5	30.1	35.9	26.7
24	72.5	42.4	30.8		
48	71.5	44.3	31.7	38.2	27.3
72	71.3	46.3	33.0		
96	71.3	47.7	34.0	40.1	28.6

The lignin was determined by the method of Ross and Potter.   The results are shown in Table V.

TABLE V

EFFECT OF pH ON THE FORMATION OF APPARENT LIGNIN

Time of pretreatment, hr.	pH of solution	Yield of pulp, %	Ross-Potter lignin in pulp, %	Ross-Potter residual lignin, %
48	2.2	66.8	50.0	34.4
48	5.0	85.2	37.6	32.0
48	8.0	82.6	36.5	30.1

If the residual lignin values reported in Table IV are plotted against the time of pretreatment, two straight lines are obtained, one for the Madison values, the other for the values obtained by the method of Ross and Potter. This is shown in Fig. 7.   Although the formation of apparent lignin, as deter-
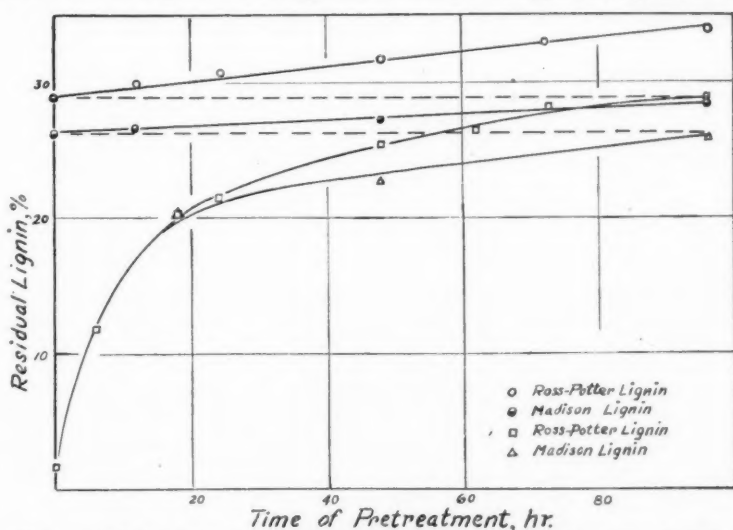

FIG. 7.   Effect of time of pretreatment (pH3; temp. 140° C.) on the formation of apparent lignin.

mined by both methods, increases linearly with time of pretreatment over
the range investigated, the amount determined by the Madison method is
much less than that determined by the method of Ross and Potter.

After 96 hr. of pretreatment the same lignin value was obtained on the
uncooked sample as that obtained (see Table III) after three hours of cooking
in bisulphite liquor, and this statement holds, irrespective of which method
was used to determine the lignin.   It appears, therefore, that pretreatment for
96 hr., under these conditions, makes subsequent delignification so slow that
no loss of lignin is apparent after three hours of cooking at 140° C.   Further,
the apparent lignin produced in the pretreatment is evidently not cooked
out in bisulphite solutions, hence there is some justification for applying a
direct correction, obtained from the apparent lignin correction curve
(Fig. 7), to the residual lignin values in Table III.   Curves of these corrected
lignin values are also plotted in Fig. 7.   The corrections do not become very
appreciable until after 24 hr. of pretreatment, so that former pretreatment
series require no correction.   However, the values in Table III are con-
siderably altered when allowance is made for the apparent lignin formed in
the pretreatment.   The results were recalculated on the corrected basis,
and are listed in Table VI.

TABLE VI

Corrected values from Table III

Time of pretreatment, hr.	Yield of pulp, %	Carbo- hydrate, %	Lignin in pulp, %	Residual lignin, %	Sulphur as	
					Per cent pulp	Per cent lignin
0	48.3	47.0	2.58	1.25	0.33	13.4
6	61.9	50.2	18.8	11.7	1.18	6.28
18	66.8	46.1	30.9	20.7	1.21	3.91
24	66.8	45.2	32.3	21.6	1.20	3.71
48	67.8	42.2	37.8	25.6	1.08	2.86
62	69.0	42.3	38.7	26.7	0.94	2.44
72	70.4	41.8	40.6	28.6	1.10	2.71
96	70.2	41.2	41.3	29.0	0.80	1.93

The variation in the quantity of apparent lignin formed during pretreat-
ment in solutions of different hydrogen ion concentration was almost linear,
as is shown in Table V.   The greatest effect was obtained with the more
acid solutions.

No attempt was made in this work to identify the substance from which the
apparent lignin was formed.   The formation of such lignin-like substances
has, however, been noted before.   Norman and Jenkins (7) found that pentose,
when treated with cold 72% sulphuric acid and boiled in dilute sulphuric
acid, yielded a quantity of material that was determined as lignin by the
accepted methods.   Hawley and Harris (5) heated Cross and Bevan cellulose,
prepared from spruce wood, in glass tubes for several days at 135° C.   Large

quantities of lignin-like material were formed, apparently from the hexosans in the wood.   The product was designated synthetic lignin because many of the characteristics of true lignin were displayed by it.

The Rate of Delignification of Wood-meal Pretreated 36 hr. at 140° C.

It was desirable to prove conclusively that wood, pretreated in an aqueous medium for long periods, could be delignified if the cooking were continued for a sufficient length of time.

A large quantity of wood-meal, the same as that used in the previous experiments, was heated in a two-litre, Allegheny metal digester for 36 hr. at 140° C. in a solution of pH 3.   Five-gram samples of this pretreated wood-meal were cooked for 3, 6, 9, and 12 hr. at 140° C. in liquor of composition: total SO_2, 5.00; free SO_2, 3.88; combined SO_2, 1.12%.   Longer periods of cooking were attempted, but the liquor decomposed after 12 hr., and sulphur was precipitated into the pulp.   Longer digestion was finally attained by cooking the wood-meal nine hours, removing the bombs, and replacing the waste liquor with fresh liquor.   The digestion could be continued for 21 hr. by this two stage process.

The results shown in Table VII indicate that the change in the lignin brought about by the pretreatment hinders, but does not prevent, subsequent cooking.   It is evident that more than 2.63% of the lignin originally present

TABLE VII

WOOD-MEAL PRETREATED IN A SOLUTION OF pH 3 FOR 36 HR. AT 140° C.

Length of cook, hr.	Yield of pulp, %	Carbo-hydrate, %	Lignin in pulp, %	Residual lignin, %	Sulphur as	
					Per cent pulp	Per cent lignin
3	69.0	46.5	32.6	22.5	1.21	3.72
6	62.6	45.0	28.1	17.6	1.35	4.81
9	54.6	42.7	21.8	11.9	1.56	7.14
12	46.3	42.0	9.3	4.32	1.40	15.0
9 + 3	49.9	42.8	14.2	7.08	0.76	5.35
9 + 6	47.4	42.3	10.7	5.06	0.57	5.31
9 + 9	44.3	41.4	7.85	3.52	0.41	5.18
9 + 12	44.0	41.6	5.98	2.63	0.31	5.26

NOTE:—*Lignin content of wood: (a) before pretreatment, 29.0%; (b) after pretreatment, 33.9%.*

in the wood must have been affected during the pretreating, yet the lignin is reduced to this value after 21 hr. of cooking, and the lignin curve (Fig. 8) indicates that longer cooking would remove more lignin.

Several interesting features are shown in this series.   It is noted that the logarithm of the residual lignin values, in the second stage of the cooking, gives a straight line.   A discontinuity is evident in the sulphur values, the
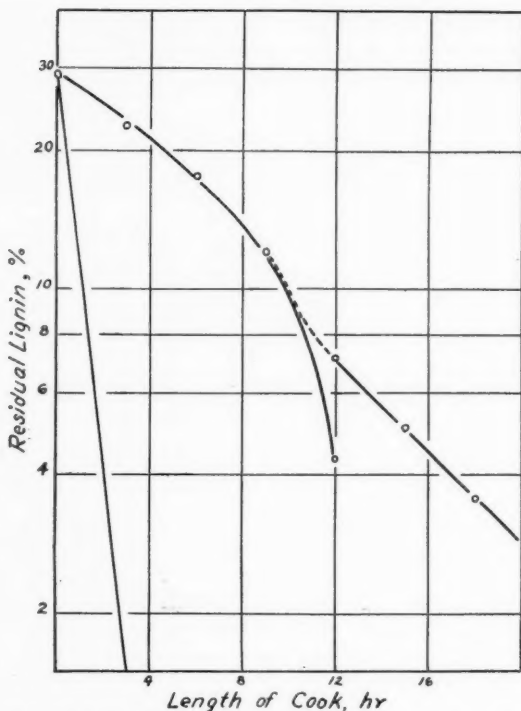
FIG. 8.   *Rate of delignification of untreated wood-meal and wood-meal pretreated for 36 hr. at pH 3 and 140° C.*

sulphur as a percentage of the lignin becoming constant in the second stage. Evidently no further sulphonation occurred after the fresh liquor was introduced, and no explanation can be advanced to explain this phenomenon. Further investigation of this discontinuity in the sulphur values would be very interesting, but no time was available to continue the experiments. The most important fact, from the standpoint of this pretreatment investigation, was that all the lignin could eventually be brought into solution, even after 36 hr. of pretreatment.

The Pretreatment of Jack Pine

Thus far the investigation of pretreatment had been confined to a study of spruce wood.   In order to determine whether this phenomenon was exhibited by other wood species, a few experiments were made with jack pine wood-meal.   A quantity of wood-meal, obtained from the heartwood, was extracted in a Soxhlet extractor with an alcohol-benzene mixture for 24 hr. and then air-dried.   Five-gram samples of this extracted wood-meal, and also of the unextracted wood-meal, were cooked in the bronze digesters for three hours at 140° C.   The composition of the cooking liquor was:

total SO_2, 5.24; free SO_2, 3.90; combined SO_2, 1.34%. The results of this experiment are compared in Table VIII with those obtained with spruce under the same conditions, and previously reported in Table III.

TABLE VIII

EXTRACTED AND UNEXTRACTED SPRUCE AND JACK PINE WOOD-MEAL, COOKED THREE HOURS AT 140° C.

Wood species	Yield of pulp, %	Carbo- hydrate, %	Lignin in pulp, %	Residual lignin, %	Treatment of sample
Jack pine	53.4	46.0	13.8	7.36	Unextracted
Jack pine	48.4	45.6	3.76	1.86	Extracted
Spruce	48.3	47.0	2.58	1.25	Unextracted
Spruce	49.1	47.9	2.46	1.21	Extracted

NOTE.—*Jack pine wood: density 0.46; lignin content, 32.6%.*

It is evident from the results in Table VIII that unextracted jack pine wood is much more slowly cooked than the extracted wood. Spruce wood, however, can be cooked equally well before extraction and after the resins have been removed. It is interesting to note also, that the solvent-extracted pine is delignified almost as rapidly as the spruce. There is some slight difference in the rates, even when allowance is made for the greater original lignin content of the pine, but this difference might easily be due to the difference in the densities of the two wood species used.

The yields of carbohydrate show a slight difference in favor of the spruce, and a greater difference would be expected if the lignin content of the pine pulp were reduced to that of the spruce pulp.

This experiment confirms Hagglund's (4) assertion that there is no difficulty in delignifying solvent-extracted pine, provided that no water-insoluble extracting fluid remains within the wood fibres.

Samples of unextracted jack pine wood-meal, and wood-meal extracted with alcohol-benzene for 12 hr., were pretreated in buffer solutions for six hours at 130° C. The samples were then air-dried, and cooked for three hours at 140° C. in sulphite liquor of composition: total SO_2, 5.11; free SO_2, 3.93; combined SO_2, 1.18%. These results are shown in Table IX.

The curves, showing the yields of pulp and the residual lignin plotted against the pH of the pretreating solutions (Fig. 9), are similar to the corresponding curves for spruce, which were shown in a previous paper (3). There is considerable difference, however, in the degree of cooking obtained with the solvent-extracted and unextracted jack pine, and spruce wood-meal. More delignification was obtained in cooking pretreated spruce than was obtained with the solvent-extracted, pretreated jack pine, but there is an almost constant difference between the lignin values for the spruce and solvent-extracted jack pine at any pH below 5. This shows that a change

TABLE IX

SOLVENT-EXTRACTED AND UNEXTRACTED JACK PINE PRETREATED IN BUFFER SOLUTIONS

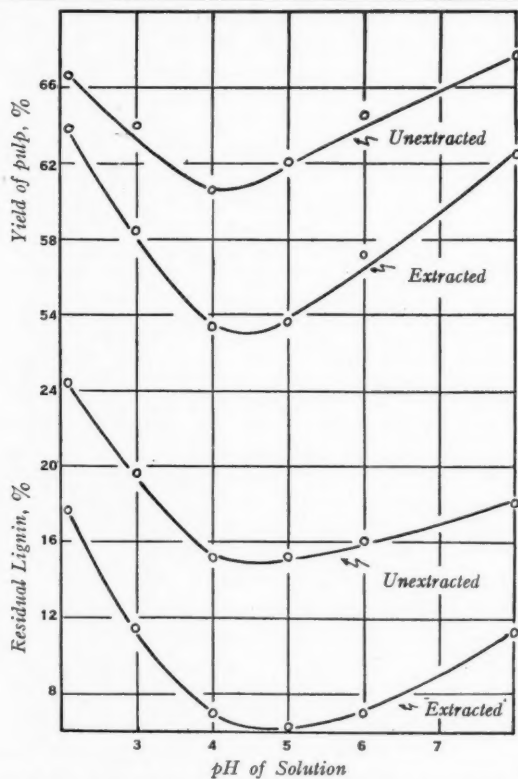| Pretreating solution, pH	Yield of pulp, %	Carbohydrate, %	Lignin in pulp, %	Residual lignin, %
A. Unextracted wood-meal				
2.2	66.6	42.2	36.6	24.4
3	63.9	44.3	30.7	19.6
4	60.6	45.4	25.0	15.1
5	62.1	46.8	24.6	15.3
6	64.5	48.5	24.6	16.0
8	67.6	49.6	26.6	18.0
B. Solvent-extracted wood-meal				
2.2	63.8	46.1	27.7	17.7
3	58.5	47.1	19.5	11.4
4	53.4	46.6	12.8	6.84
5	53.7	47.5	11.6	6.25
6	57.2	50.2	12.2	6.98
8	62.5	51.2	18.0	11.30

FIG. 9.   *Effect of pH of pretreatment at 130° C. for six hours on subsequent delignification of jack pine wood-meal.*

in the hydrogen ion concentration of the pretreating solution had an equal effect on both the spruce and jack pine lignin. The agreement is not so close at pH values above 5.

The curves also indicate that a change in the hydrogen ion concentration of the pretreating solution does not alter the rate of delignification of unextracted jack pine as much as it does that of extracted jack pine or spruce. A possible explanation for the above results lies in the difference in the rate of penetration of liquids into solvent-extracted and unextracted pine wood. De Montigny (6) found that some substances existed in jack pine which hindered the penetration of liquids into the wood. When these substances were removed, by extracting the chip with organic solvents, the rate of penetration was greatly increased. The presence of resins, fats, and waxes in the wood fibres may hinder the diffusion of the buffer solution to the lignin surface, and also the diffusion of the cooking liquor. If this were true, the acids formed in the fibres during pretreatment would have considerable effect in determining the hydrogen ion concentration in contact with the lignin particles, and would modify the influence of the buffer solutions. This factor would have a more noticeable effect the more the pH of the buffer solution differed from that due to the acids formed in the wood, and the lignin curve would rise less steeply on either side of the minimum.

Since the minimum in the pretreatment curves for both spruce and jack pine occurs at the same pH, there appears to be no fundamental difference between spruce and jack pine lignin. The curves for the jack pine are merely displaced upward, owing to a slower rate of cooking, which might easily be explained by differences in the wood structure, and the nature and quantity of the resins in the two wood species.

Discussion

Reference has already been made to the hypothesis that lignin may coagulate when heated in aqueous media, and that this tendency of the lignin to coagulate may exert considerable influence during the normal cooking process. The writers of course realize the possibility of the alternative hypothesis that the lignin may be altered chemically during pretreatment in such a way that subsequent cooking is rendered more difficult. At this point it is therefore desirable to assemble the salient facts for a general consideration, and to discuss their relation to the hypotheses mentioned above.

It has been demonstrated that when wood is heated in aqueous media it becomes very difficult to delignify in bisulphite solutions. The hypothesis has been advanced that the lignin, existing in the wood as submicroscopic particles, or even as thin films upon the cellulose fibres, may tend to agglomerate under these conditions to form a smaller number of relatively larger particles. Such a coagulation would result in a great decrease in the lignin surface, and, since the lignin is in the solid phase, the reaction with solvent solutions might be confined to this surface. The rate of the reaction would thus be decreased.

The fact that the rate of delignification of wood in sulphite liquor approximately obeys the law of a first order reaction, in spite of all the variable factors concerned, is difficult to explain on the basis of chemical reactions. One would expect the rate to increase beyond that given by a first order reaction as sulphonation becomes more complete, and also that the liberation of acids into the solution would increase the rate of hydrolysis. The conception of a tendency for the lignin particles to coagulate, and thus oppose the cooking action, which tends to decrease the size of the lignin particles, offers a ready explanation for the nearly straight line relation observed. Further, the curves of rate of delignification (see Fig. 8) of pretreated wood are of the shape one would expect on the basis of the above considerations. Thus, if the lignin particles are considered to have been coagulated by the preliminary treatment, a gradual increase in the cooking rate, such as was observed, would be expected as the particles become smaller in size owing to the cooking reaction. The reaction at the surface of these particles would finally reduce them to a size comparable to that of the lignin particles which are present in an ordinary cook, and the rate of pulping should then be the same as in cooking untreated wood. The curves in Fig. 8 illustrate this point, for after about 12 hr. of digestion the rate curve for the pretreated wood becomes virtually parallel with the curve for the untreated wood.

A coagulation of the lignin particles might affect the cooking rate in two ways; namely, by decreasing the rate of sulphonation, and by decreasing the rate of hydrolysis. The rate of sulphonation has been proved to be decreased by heating wood in aqueous solutions, and there is evidence that the rate of hydrolysis is also decreased. This is indicated by the logarithmic curves of the delignification rates for pretreated and untreated wood (Fig. 8). After one hour of cooking the sulphur value, as percentage of lignin, for the untreated wood, is equal to the sulphur value obtained after six hours of cooking with the pretreated wood: namely, 4.81%. The slopes of the two curves, however, are vastly different at these points, the rate of delignification being much less in the case of the pretreated wood. It is possible that, in the case of the pretreated wood, all the sulphur may not be taken up in such a manner as to assist in the dissolving of the lignin, but there is no reason to believe this to be true, whereas a decrease in the rate of hydrolysis would appear to be the logical consequence of a decrease in the exposed surface of lignin.

Calhoun and Maass (1) have found evidence that the effect of neutral salts in the pretreating solution is in the order of the lyotropic series for the swelling of wood. This suggests that the loosening of the wood structure by swelling may allow the lignin particles a greater mobility, and hence increase the ease with which a number of particles may gather together to form one large particle. Swelling may thus be involved in the pretreatment of wood in buffer solutions. Little is known about the effect of pH on the swelling of wood at high temperatures, although pH has no effect on the swelling of wood at room temperature except in very alkaline solutions (9).

The minimum in the curve of pH of pretreatment may, however, be due to some entirely different cause, either from the standpoint of a physical or a chemical change in the lignin. And the fact that a minimum is obtained does not provide much evidence in favor of either hypothesis. Similarly, the effect upon the rate of delignification of increasing the temperature or the time of pretreatment can be explained equally well as a chemical polymerization, or as a physical coagulation of the lignin particles. It should be emphasized, in this respect, that the physical process cannot be considered as gel formation, which takes place when the temperature is lowered, for the lignin particles are already in the form of a gel, but the heating of lignin in aqueous solutions might cause coagulation somewhat analogous to the coagulation of albumin under the influence of heat. The time and temperature of pretreatment might also control the extent of the coagulation, through determining the mobility of the lignin particles. Any factor that tends to loosen the wood structure would be expected to allow the particles greater freedom of movement.

If the effect of pretreatment is a chemical polymerization that blocks the group to which the bisulphite ion adds, the process must be considered reversible. Such a process is possible, but does not lend itself so readily to an explanation of all the experimental results. Thus far the greater part of the evidence seems to favor a colloidal change that leaves the lignin unaltered chemically, inasmuch as it can be completely dissolved by the action of sulphite liquor, although at a reduced rate of pulping. Some chemical change, however, is a definite possibility that should not be ignored, and further investigation of the problem may reveal definite evidence in favor of such a change.

References

1. CALHOUN, J. M. and MAASS, O. Can. J. Research, B, 15 : 80-83. 1937.
2. COREY, A. J. and MAASS, O. Can. J. Research, B, 13 : 149-155. 1935.
3. COREY, A. J. and MAASS, O. Can. J. Research, B, 13 : 289-295. 1935.
4. HÄGGLUND, E. Cellulosechem. 8 : 25-31. 1927.
5. HAWLEY, L. F. and HARRIS, E. E. Ind. Eng. Chem. 24 : 873-875. 1932.
6. DE MONTIGNY, R. Ph.D. Thesis, McGill University. 1934.
7. NORMAN, A. G. and JENKINS, S. H. Nature, 131 : 729. 1933.
8. ROSS, J. H. and POTTER, J. C. Pulp Paper Mag. Can. 29 : 569-571. 1930.
9. STAMM, A. J. J. Am. Chem. Soc. 56 : 1195-1204. 1934.
10. YORSTON, F. H. Project 70 M., Prog. Rept. No. 4. Forest Products Laboratory, Montreal. 1935.